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Interim Annual Report

DEVELOPMENT OF UNIFORM AND PREDICTABLE BATTERY MATERIALS FOR NICKEL-CADMIUM AEROSPACE CELLS

(8 September 1969 – 7 September 1970)

Contract No.: NAS5-11561

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Prepared by

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Bear Hill
Waltham, Massachusetts 02154

for

Goddard Space Flight Center
Greenbelt, Maryland 20771

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Goddard Space Flight Center

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ABSTRACT

This report describes studies of the impregnation of nickel plaque to form nickel cadmium battery plates. Three basic processes were examined: (1) chemical conversion of the nitrates to the hydroxides, (2) the method first described by Fleischer, and (3) electrochemical conversion at 25 °C. The aim was to define the procedures and preparative conditions that would give rise to the most uniform components in a reproducible manner.

The variables considered were solution concentration for chemical conversion, current density for the Fleischer method, and the loading for both methods. These variables were chosen for more detailed study from a previous preliminary examination of impregnation methods. The plates were examined in terms of uniformity and reproducibility of weight gain, capacity, and utilization. The determination of utilization demanded chemical analysis of the active materials. Since analytical procedures are not well defined in the literature, significant effort was devoted to the development of reproducible and accurate analytical methods.

For negative plates, both the charged and discharged forms of the active material are readily determined since the ionic form [$Cd(OH)_2$] dissolves readily in ammoniacal NH_4Cl whereas cadmium metal is unaffected. After separation, the two forms of cadmium are determined by EDTA titration.

A similar approach to the analysis of the positive electrode resulted in significant errors due to corrosion of the nickel substrate. A novel approach involving potentiostatic control of the plate during the extraction process successfully eliminated the corrosion problem, but its application is limited to analysis of the plate in the discharged state. For this reason and because both the charged and discharged species are soluble in any extraction solution, a separate determination of the state of charge is necessary. The method used depended on the determination of the active oxygen equivalent by reaction with potassium iodide and subsequent estimation of the iodine formed with sodium thiosulphate. It was established that it is critically important not to wash and dry the electrodes prior to analysis. Plaque corrosion is also another potential source of error in this determination. Specific techniques are described to minimize these errors. However, even with these precautions, determination of the state of charge by a chemical method still gives a figure lower than that defined by discharge. It is concluded, therefore, that the only guide to utilization of positive active material is a measurement of the amount of material that is not discharged (in terms of residual active oxygen) when the plate is in the nominally discharged state.

It was concluded from the experimental data collected on the impregnation methods that more uniform and reproducible plates were prepared by the chemical conversion process. For the positive plates, the less concentrated impregnation solution are to be preferred. No distinction could be drawn for the negatives. Plates prepared by the electrochemical process were noticeably lower in reproducibility and uniformity.

It should be stressed, however, that these are interim assessments, based on capacities measured after up to ten cycles and have not included factors such as cycle life or behavior under sealed cell conditions.

It is also apparent from the data that uniformity and reproducibility of weight gain and capacity improve with loading, suggesting that there is a leveling effect (as might be expected). More surprisingly, utilization was found to be independent of loading up to quite high levels. From a limited amount of data, plaque thickness was found to have no influence on uniformity. Plaque corrosion during impregnation was more extensive for the chemical conversion process.

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I. INTRODUCTION

The aim of this program is the definition of a systematic procedure for producing uniform components for nickel cadmium cells. The first phase (described in earlier reports)[1] emphasized the production of uniform porous nickel plaque for both loose sintering and a slurry coating process, and the development of experimental techniques to identify uniform physical characteristics. Of the two processes, the slurry coating process is preferred for production of plaque to be used in a study of the factors considered important in the impregnation of plaque with active materials to produce battery plates.

This second phase of the program has considered the methods by which the active materials are incorporated into the nickel plaque to produce both positive and negative plates. The active material for the positive plate is precipitated as nickel hydroxide and for the negative plate as cadmium hydroxide. The purpose of the study of the various methods of impregnation described here is to determine which one offers the best control of the quantity and distribution of the active materials in the pore structure. Good distribution and also optimum morphology are important to effective utilization of the active material. In the absence of good utilization, uniform operational characteristics over an extended cycle life are probably not attainable.

The basic methods for impregnation rely on the conversion of soluble salts of nickel or cadmium into the insoluble hydroxides in the pore structure of the nickel plaque. Various methods are used to effect the conversion. The most widely used is straightforward chemical conversion.[2] After vacuum impregnation with nickel or cadmium nitrate, the plaque is dried and then immersed in hot potassium hydroxide. The process is repeated several times until the required loading is achieved. The method, documented by Fleischer,[3] involves a variant of the chemical conversion process in which substantial cathodic currents are applied to the plate during the immersion in potassium hydroxide. For this procedure, the plates are not dried after impregnation with nitrate. The cathodic current produces a rapid increase in pH in the pore structure by reduction of nitrate and thereby localizes the precipitation of the hydroxide. For the negative plates, the cathodic current also converts some of the hydroxide to metallic cadmium. Because this has a lower specific volume than cadmium hydroxide, there is a greater void volume in the plate for the next impregnation cycle. A third method, also used commercially, is based on vacuum impregnation with a very concentrated solution

of nickel nitrate. This solution is produced by dissolving the nitrate in its own water of crystallization at a temperature of about 65 °C. (For this reason, the method is sometimes described as molten salt impregnation.) The nitrate is then partially thermally decomposed to a hydrated oxide before immersion in potassium hydroxide to complete the conversion to the hydroxide. The greater quantity of nickel salt introduced into the plaque structure in this approach means fewer impregnation cycles for a particular loading.

A further method by which the conversion may be effected is purely electrochemical.[4,5] The plaque is cathodized in 2M nickel or cadmium nitrate. The local increase on pH in the plaque structure brings about the precipitation of the hydroxide.

As stressed previously, precipitation of the active materials in the pore structure does not necessarily mean that they can be effectively utilized in the charge discharge process. In any assessment of plate performance, it is therefore quite important to define the utilization of the active materials. For this reason, considerable effort in this program was devoted to defining analytical techniques to determine the quantities of active material that were actually cycling. For the negative plate, it will be demonstrated that this is a straightforward process, but the combination of nonintegral stoichiometry and Faradaic inefficiency of the positive plate makes the latter a much more complex problem.

This report describes the analytical methods that were developed, the procedures used in the impregnation processes, and presents a comparative survey of the results obtained.

II. CHEMICAL ANALYSIS OF NiCd BATTERY PLATES

A. Introduction

Two criteria are normally used to assess the effectiveness of impregnation processes: (1) weight gain, and (2) capacity. For the objectives of this program, these two figures alone are not considered to be sufficient characterization to ensure uniform behavior, particularly as function of cycle life. The problem is associated with the inefficiency of the charge-discharge processes, which can be a function of the morphology of the active materials or their distribution in the plaque structure on a microscopic scale,* i.e., the conditions prevailing during impregnation. The inefficiency may be real in that there is a secondary Faradaic process (e.g., O_2 evolution on charge) or apparent when some of the active material does not cycle. This latter behavior can be a result of electrical isolation, chemical changes, or passivation. It is, therefore, desirable to be able to identify those areas of the plate that do not cycle efficiently in order to be able to identify truly uniform behavior. This information can be obtained by careful chemical analysis of the active materials. It is, of course, necessary to be able to identify the charged and discharged states independently. This is relatively straightforward for the negative plates, but is quite complex for the positives. Before these problems can be discussed, it is worthwhile to examine the nature of the active materials in detail.

The positive active material in the discharged state is well characterized as divalent hydroxide. $Ni(OH)_2$ is isomorphous with the cobalt compound, $Co(OH)_2$, and has a lattice of the CdI_2 type.[6] This is a layer structure in which every Ni atom is surrounded by six hydroxyl groups. Every hydroxyl group in turn forms three bonds to Ni atoms in its own layer and, at the same time, is in contact with three hydroxyls of the adjacent layer. $Ni(OH)_2$ generally contains varying amounts of water up to $Ni(OH)_2 \cdot 1.5\ H_2O$.

A significant advance was made when Bode, et al.,[7] following work of Feitknecht,[8] were able to identify the hydrated and nonhydrated forms of the discharged material by differences in the X-ray patterns. The two forms, $Ni(OH)_2$ and $Ni(OH)_2 \cdot 1.5\ H_2O$, are designated β $Ni(OH)_2$ and α $Ni(OH)_2$, respectively. The α $Ni(OH)_2$, on oxidation, gives an X-ray pattern

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*Macroscopic deviations in the distribution would be apparent from an analysis of the weight gain per unit area of different regions of the plaque.

identical in all respects to that of γ NiO · OH* reported by Glemser and Einerhand.[9] The water of hydration is assumed to be occluded in the layer lattice, increasing the layer separation and thereby giving a distinctive X-ray pattern. The α $Ni(OH)_2$ either occurs as the freshly precipitated form of the active material or in the discharged state after cycling which has involved extensive overcharge, i.e., the normal cycling mode (including overcharge) in a sealed cell, in descriptive terms, is between the γ NiO · OH and α $Ni(OH)_2$.

The β $Ni(OH)_2$ which is formed by aging of the α form (drying plates at elevated temperatures accelerates this change) gives, on oxidation, the trivalent nickel oxide β NiO · OH; overcharge then brings about a gradual change to the γ NiO · OH. The γ form, which exists in an oxidation state greater than three, then generates the α $Ni(OH)_2$ on discharge. The continued presence of α $Ni(OH)_2$ in a plate on cycling is, however, dependent on extensive overcharge in each cycle. Cycling without overcharge is between the β forms of both the charged and discharged state.

It has been suggested that the higher oxides derived are stabilized by the presence of positive ions between the lattice layers,[10] e.g., $[Ni_3O_3(OH)_3]$ $(OH)_2K$, where K^+ occupies an "interstitial" position in the layer lattice structure equivalent to the position of the water in α $Ni(OH)_2$. The stability of the higher valence forms of γ-NiOOH is dependent on the presence of concentrated alkali electrolyte. The distribution of potassium in charged positive active material has been confirmed by the electron microprobe studies of Kober.[11]

At normal temperatures, the charged hydrated form (γ NiO · OH) is stable, probably because of hydrogen bonding. Infrared measurements[12] show hydrogen bonding of OH groups in the lattice, but these bonds are absent in the completely discharged state. Dehydration of the divalent α $Ni(OH)_2$ can therefore occur relatively easily[13] and, according to Bode,[14] irreversibly in concentrated KOH at elevated temperatures.

The exact nature of the charge-discharge mechanism is still a matter of dispute.[15, 16] One view is that the charging process may be regarded simply as the replacement of OH^- in the lattice of O^{2-}, which involves proton migration only. However, the determination of the overall stoichiometry and measurements of the reversible potential imply that the transition that should be considered is:

$$Ni(OH)_2 + H_2O \rightarrow NiO \cdot OH + H_3O^+,$$

where the water involved is in the lattice structure but not necessarily linked in any strict stoichiometric relationship to the nickel atoms.

For this mechanism, the mobile species would be H_3O^+, probably as proton migration and separate diffusion of water. The rate of diffusion of water is likely to depend on the interlayer lattice separation. The nature of the positive active material is then dependent on its crystalline form, which in turn depends on the conditions of precipitation and the charge-dis-

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* The notation of α $Ni(OH)_2$ for the hydrated discharged state and γ NiO · OH for the related charged form will be retained in this presentation to remain consistent with the original literature. Tuomi uses "α phase" to designate the γ-nickel hydroxy-oxide of Glemser and Einerhand.

charge cycles. Most probably the charge-discharge process depends on cycling between β $Ni(OH)_2$ and β NiOOH but in the presence of extensive overcharge the γ form of NiOOH is formed. (In the complex pore structure of a battery plate, it is probably that some regions, e.g., close to the surface, go into overcharge conditions before the full-rated capacity is reached. This is because of the influence of the distribution of current density in the pore structure on local potential differences.)

The nature of the negative active material is more straightforward — the charged state is metallic cadmium and the discharged state is $Cd(OH)_2$, i.e., there is no problem in defining stoichiometry. Two crystalline forms of $Cd(OH)_2$ exist: the C_6 form, and a form fairly recently identified by Glemser, Hauschild, and Richert[17] and called γ $Cd(OH)_2$. Glemser, et al., prepared γ $Cd(OH)_2$ by the hydrolysis of cadmium dimethyl, but there are indications that γ $Cd(OH)_2$ can be precipitated under certain impregnation conditions particularly at low temperatures. Gottlieb[18] and Okinaka and Whitehurst[19] have described circumstances in which charge acceptance in the first cycle at low temperatures is markedly decreased compared to normal temperature operation, but recovers in subsequent cycles. From this we may infer that the characteristics of $Cd(OH)_2$ are quite dependent on the conditions under which it is precipitated. This could apply equally well to the chemical precipitation during impregnation as to the "electrochemical precipitation" during discharge.

In the analysis of nickel cadmium battery plates, therefore, the components we are interested in are Cd°, Cd^{2+}, and Ni° (plaque) in the negative plate; and, at the positive, Ni^{2+}, $Ni^{(2+x)+*}$, K^+, H_2O, adsorbed or occluded O_2 and the nickel metal of the plaque. Clearly the positive plate is a much more complicated problem.

Analysis of the negative plate is readily carried out by selective dissolution of cadmium hydroxide with subsequent determination of the amount dissolved by complexometric titration. The metallic residue of cadmium and nickel may be dissolved in nitric acid and the two components of the solution determined again by complexometric titration. Analysis is uncomplicated except for the electrodes close to being fully charged that are difficult to wash and dry without oxidation.

For the positive plate in the green state (prior to formation), the components are Ni^{2+}, Ni°, and water. As will be demonstrated, analysis at this stage is straightforward if certain precautions are taken. In the charged state which is characterized by nonintegral stoichiometry, the value of x in $Ni^{(2+x)+}$ can range from one to nearly two.* Determination of the value of x poses a particular problem in that the highest valent states are stable only in the presence of KOH at the particular concentration at which they were formed. Any dilution of the electrolyte prompts a self-discharge reaction coupled with the evolution of oxygen. Thus, although sophisticated methods have been described for determination of the state of charge, e.g., infrared absorption intensities,[12] these do not represent the true value in situ because washing and drying is a necessary precursor to the measurement. This factor will be examined in more detail below. In the discharged state, the value of x is never zero, i.e., the plate

* $Ni^{(2+x)+}$, represents the nonstoichiometric charged state of the positive plate.

cannot be reduced to a uniquely divalent state. Knowledge of the value of x in the discharged state is essential to define the behavior for plates prepared under different circumstances. Its determination by any of the methods to be discussed is relatively straightforward since the complication of the self-discharge process does not exist.

The residual valence in excess of two can, however, present problems in determining the total quantity of active material in the plate. This occurs because all the methods of determination depend on dissolution by complexation of the nickel in ionic form while leaving the metallic nickel substrate unattacked. However, the substrate is readily attacked in the presence of an electroreducible species such as the residual charged material in the following manner. The presence of residual charge is probably a result of isolation by the completely discharged state $Ni(OH)_2$, a poor electrical conductor; but, as the source of isolation is dissolved, the electroreducible species is exposed. Simultaneously, the passive film protecting the nickel substrate, which is an ionic form of nickel, is also dissolved. Local cell action between the charged material and the nickel substrate can result in dissolution of the nickel substrate, resulting in a significant error in the determination.* As will become apparent, the error is compounded in any attempt to determine the constitutional water in the active material.

The problem of corrosion of the substrate does not occur in the analysis of the negative plate since the rest potential in both the charged and discharged state is below that at which nickel dissolution can occur.

It is worthwhile to examine the published work in this field. In most cases, the objective was a better understanding of the mechanism of the nickel electrode and of the nature of the positive active material. The analytical chemistry was for the most part only one facet of the study. In this context, the comments are quite enlightening as far as the practical problems are concerned.

Tuomi[20] in a study of the mechanism of the positive active material of pocket plate batteries made X-ray diffraction measurements paralleled by chemical analysis to determine the active oxygen content (the charged state of the positive electrode may be considered as bound active oxygen usually denoted [O]).[21] For both the X-ray measurements and the chemical analysis, it is stressed that the samples were not washed free of alkali. In the case of the X-ray measurements, the samples were allowed to dry (with the KOH being converted to carbonate) and the nickel flake was removed magnetically. The chemical analysis for active oxygen was carried out by reaction with arsenious oxide and back titration with $KMnO_4$ without washing, and apparently, without removal of the nickel flake. As stated by Tuomi, "Samples were not washed free of electrolyte since this generally caused a slight decrease in valence state as well as decreasing the analyzed nickel content of the sample." In a further comment, when considering the more rapid rate of reaction with alcohol of an electrode directly after removal from the cell, compared to one that had been dried, Tumoi states that, "It appears certain that the valence state of 3.48† is appreciably less than is possible with α* phase at the end of electrolysis."

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* See footnote, Page 4.

† This number corresponds to the (2+X) figures quoted on the previous page.

Kober,[12] in his studies of positive plates by infrared spectroscopy, worked with impregnated sintered plates. Samples were prepared for spectroscopic analysis by grinding. To test whether this process altered the electrochemical activity of the sample, the powder was discharged in a pocket plate electrode and the capacity compared with a similar sintered plate. (The sintered plate was subjected to the same drying process as the powdered material.) A 25% loss in capacity was observed. Kober considered this effect to be minor from the point of view of his investigation, but it is obviously significant in any quantitative determination of the state of charge and must rule out any process that demands drying of the plate.

Aia[21] in a study of structure and stoichiometry of nickel hydroxides developed an elegant method of determining the total active material in a sintered plate using a magnetic balance. Active oxygen was determined by the iodine-thiosulphate method. According to the experimental section of the paper, the determination was carried out on dried powdered electrode material. However, for the correlation with capacity measurements, determination of active oxygen was carried out on unwashed electrodes and without the separation from metallic nickel. (Particular care is needed in carrying out the iodine-thiosulphate estimation in the presence of metallic nickel. This is discussed in the context of Harivel's work below.) Aia also noted that 80% of the active oxygen was lost in 1 hr on washing in a continuous extractor with boiling water.

Wynne Jones,[22] and Conway and Sattar[23] have used analytical techniques to examine thick films of nickel oxide on nickel. Conway considered that the iodometric determination used by Wynne Jones presents difficulties and notes that the metallic nickel dissolves in the acidic medium. (Bro and Cogley[24] state that the pH range must lie between 1 and 2. Above pH 2, it was found that the higher nickel oxide was not completely reduced.) It is more likely, however, that dissolution of nickel is a result of interaction with the tri-iodide ion than a direct attack and is thus a serious source of error in the active oxygen determination. Conway's approach was to determine the extent of oxidation of an ammonical solution of hydrazine (by back titration with permanganate) by the electrode in the charged state. Careful deoxygenation was necessary to minimize the oxidation of metallic nickel. For extensive reaction times, catalytic decomposition of hydrazine to ammonia was observed. Principally for this latter reason, Conway considered the method unsuitable. The iodide method was also termed unsatisfactory. A method for determining total nickel content of the active material is, however, described by Conway in which higher valent states are reduced in hydrazine prior to dissolution in KCN to be determined spectrophotometrically.[25] Correction curves for the loss of metallic nickel as a function of immersion time in both hydrazine and the cyanide were obtained under conditions where oxygen was extremely carefully excluded from the system. (Extrapolation of these figures obtained for thin films on a wire to a sintered plaque 0.030 in. thick, 80% porous and a typical surface area of 0.12 m^2/g would result in a 2% weight loss of metallic nickel in 1 hr. For most plate extractions, it is unlikely that oxygen could be effectively kept out of the system, so that the losses could be higher.)

Harivel[26] introduced a modification to the iodine thiosulphate approach to determine rates of self discharge of active oxides formed at different charge rates and subject to different thermal treatments. In his method, the iodine liberated by the active oxygen was titrated against thiosulphate almost immediately. The thiosulphate was added 5 ml at a time, and the time interval to the reappearance of the yellow color of the iodine noted. This technique should prevent interaction between the tri-iodide ion and the metallic nickel and eliminate the potential error in the active oxygen determination.

Kroger[27] has recently presented methods for the determination of active oxygen and total nickel content of positive active material. The active oxygen measurement depends on reaction with a solution of ferrous ammonium sulphate. Since this method demands washing (and in Kroger's description vacuum drying) of the electrode, it is subject to the criticism presented above that the figure obtained bears no relation to the real state of charge in the cell. The determination of total nickel was carried out by leaching with acetic acid in the presence of hydrazine sulphate.

B. Negative Plate Analysis

The discharged state of the negative plate $Cd(OH)_2$ (or CdO) may be extracted from a sintered plate using Muspratt solution.* Metallic cadmium is unaffected, as is the nickel plaque at the rest potential of the cadmium electrode. The plates previously washed and dried out of contact with air and containing approximately 1 g $Cd(OH)_2$ were immersed in 200 ml of Muspratt solution at 70 to 80 °C and stirred occasionally. Additional ammonium hydroxide was added to the solution periodically to make up evaporative losses.† After 1 hr, the extraction solution was replaced, the original solution being retained in a volumetric flask. When no further weight loss was observed (as was always the case within a total of 2 hr extraction time), the plaque was removed and the extraction solutions combined. The total cadmium content of the extraction solution was then determined by titration against EDTA using Eriochrome Black T as the indicator.

The nickel plaque containing metallic cadmium was then completely dissolved in nitric acid. After the evaporation of most of the acid, the residual solution was dissolved in 100 ml water and adjusted to pH 10 by the addition of NH_4OH. The total cadmium was then again determined by EDTA titration. The following procedure is necessary to determine cadmium in the presence of nickel. Both the cadmium and the nickel are first complexed with sodium cyanide by adding 10 mil of 10% NaCN to 10 mil of the original solution. At this time, the addition of Eriochrome Black T gives a blue color. Approximately 10 ml of formaldehyde was then added to break the cadmium cyanide complex to produce a deep red color. (Under these conditions,

* The composition of Muspratt solution is defined in Appendix I.

† This is particularly important in the analysis of plates containing a nickel plated iron substrate, to prevent dissolution of the iron. In other respects, the analytical procedures described in this report are applicable equally well to plates on both nickel and iron substrates.

the nickel remains complexed.) The free cadmium was then titrated against EDTA, the end point being denoted by a purple color. The complete experimental procedures involved in negative plate analysis are presented in Appendix I.

Typical analyses are listed in Table I. The first column lists the weight/unit area of the plate after impregnation. Separate determination of $Cd(OH)_2$ and Cd by the technique described above gives the figures listed in columns 2 and 3. In order to assess the accuracy of these measurements, we may combine them to give a total weight of active material. Subtracting this from the original plate weight (column 1) will give a figure for the weight/unit area of the plaque (column 6). This can be compared to the measured weight/unit area of the plaque prior to impregnation (column 7). Good agreement is obtained even though six separate physical measurements are involved. There is an indication of a small systematic error in that values (with one exception) recorded in column 6 are higher than in column 7. It is worth noting the importance of chemical analysis of assessing plate uniformity. For the first two samples, there is a 4% difference in the total weight of active material as cadmium plus cadmium hydroxide, but the agreement is better than 1% when measured as total Cd content. The figures also indicate that there is little corrosion of the nickel plaque in the impregnation of negative plates by the Fleischer method. Since no extensive efforts were required to develop the techniques to a satisfactory level of accuracy, no further results will be catalogued here.

C. Positive Plate Analysis

The principal problem in positive plate analysis, as discussed in the introduction, is to ensure complete extraction (separation) of the active material from the nickel plaque without simultaneously dissolving the plaque. In the presence of air or any active material in the charged state, the rest potential of the plate is such that the dissolution of metallic nickel is prevented only by the presence of a passive film of nickel oxide. Since the common methods of extraction of the active material, using complexing reagents, also result in dissolution of the passive film, corrosion of the nickel substrate is a very real potential error in the determination.

To assess the practical significance of the problem, we examined the straightforward application of the Muspratt extraction technique, as described by Moore,[28] to physical mixtures of $Ni(OH)_2$ and carbonyl nickel powder of well defined composition. The $Ni(OH)_2$ was carefully dried. X-ray determinations indicated that it contained no water.

The analysis was carried out as follows. The extraction of solution was prepared by dissolving 10 g ammonium chloride in 250 ml of distilled water and the solution warmed to 80° C. Seventy-five ml of 28% ammonium hydroxide was then added. The sample was immersed in the extraction solution and the temperature maintained at 80° C. The extraction of active material was allowed to proceed for 3 hr. Approximately 25 ml of 28% ammonium hydroxide was added for each hour of the extraction. The whole process was then repeated several times with fresh extraction solution until no further coloration was observed. Finally the sample was washed, dried, and weighed. The amount of active material was determined from the net weight loss. The results obtained for mixtures containing 40 and 50% nickel

Table I. Check on Analytical Methods for Negative Plates

(1)	(2)	(3)	(4)	(5)	(6)	(7)
			Total Weight of Active Material, g/cm^2			
Plate Weight g/cm^2	$Cd(OH)_2$, g/cm^2	Cd Content, g/cm^2	(2 + 3) As Cd + $Cd(OH)_2$	As Cd	(1 - 4) Plaque Weight g/cm^2	Plaque Weight Prior to Impregnation, g/cm^2
0.233	0.038	0.017	0.056	0.047	0.177	0.170
0.226	0.026	0.027	0.053	0.047	0.163	0.165
0.298	0.079	0.048	0.127	0.119	0.171	0.167
0.298	0.058	0.070	0.128	0.114	0.171	0.167
0.343	0.122	0.045	0.167	0.138	0.176	0.166
0.332	0.138	0.026	0.164	0.132	0.169	0.165
0.358	0.108	0.081	0.189	0.164	0.168	0.165
0.360	0.114	0.077	0.191	0.165	0.169	0.165
				Mean values:	0.170	0.166

hydroxide and for 100% nickel powder are given in Table II. (The 40 and 50% mixtures are close to the ratio of active material to nickel plaque in a typical positive electrode.) The observed weight loss for both the 50% mixtures examined gave an apparent active material content of 60.1%. For the mixture containing 40% active material, the apparent content was 50.0%. In both cases, there is a positive error of approximately 10% which must be attributed to corrosion of the nickel. The weight losses for the two samples of pure nickel powder exposed to the extraction solution for the same period of time resulted in substantial weight losses, 14% for the Type 287 powder and 18.4% for the higher surface area Type 255 powder. Reduction of the surface oxide in H_2 at 600 °C showed only a 1.3% loss in weight. The lower percentage weight losses observed for the physical mixtures, as opposed to the pure nickel powders, are probably a result of masking of the nickel surface by the finely divided $Ni(OH)_2$. This effect would result in some protection of the nickel substrate in a positive plate, but it is still considered that the corrosion would be significant.

Table II. Analysis of Physical Mixtures of $Ni(OH)_2$ and Carbonyl Nickel Powders

Sample	Method	Apparent Wt % $Ni(OH)_2$
50% $Ni(OH)_2$, 50% Ni (287)	Muspratt	60.1
50% $Ni(OH)_2$, 50% Ni (287)	Muspratt	60.1
50% $Ni(OH)_2$, 50% Ni (287)	Muspratt	60.1
40% $Ni(OH)_2$, 60% Ni (287)	Muspratt	50.0
		Weight Loss
100% Ni (287)	Muspratt	14.0
100% Ni (255)	Muspratt	18.4
100% Ni (255)	Reduction in H_2 at 600 °C	1.3

A further criticism of the method is that, since the stoichiometry of the active material is ill-defined (particularly after it has been cycled), and since the active material contains an unknown quantity of water the true nickel content of the active material cannot be determined accurately. This number is essential to a calculation of charge efficiency or utilization.

Also in these preliminary studies, measurements were carried out on positive plates (in the discharge state) removed from an aerospace cell, but in this case the extraction solution was 0.5% KCN out of contact with air. This extraction process is based on a method due to Brummet and Hollweg[25] for the determination of oxide films on nickel. It has the advantage that

the quantity of nickel in solution is very conveniently determined spectrophotometrically, as the cyanide. The ultraviolet absorption at 286 mμ obeys Beer's law over a wide range of concentrations. However, the weight losses observed in the extraction process never reached a plateau value, i.e., continuous corrosion of the nickel substrate occurred resulting in values as high as 63.4% (see Table III) for the active material. "Subsequent analysis of similar plates under conditions where nickel dissolution could not take place showed an active material content between 35 and 45%." Two extractions carried out with Muspratt solution also showed high values for the weight loss.

Table III. Analysis of Positive Plates from Aerospace Cell

Sample No.	Extraction Method	Extraction Time, Hr	Weight Loss, %
1a	KCN	4	49.0
1b	KCN	30	63.4
2a	KCN	4	48.9
2b	KCN	25	54.2
3	Muspratt	4	55.4
4	Muspratt	4	54.5

Exclusion of air from the solution during the extraction of these positive plates did not produce a significant difference in the weight percent loss. This was attributed in part to the presence of adsorbed oxygen on the high surface area active material and to the fact that the positive active material can never be discharged completely to the divalent form. (The undischarged material becomes activated as the protective film of $Ni(OH)_2$ is dissolved during extraction.) The straightforward Muspratt extraction or extraction with KCN is therefore considered an unsuitable method of determination of the active material in the positive plate.

Two modifications to the method were considered. The first of these was to carry out the extraction in the presence of a reducing agent that would in theory, remove the electroreducible species which are a necessary adjunct to the nickel corrosion process.

The materials examined were hydrazine and sodium borohydride. In the first case, the hydrazine was found to be ineffective possibly because of the high pH of the Muspratt solution. A separate pretreatment with hydrazine at lower pH followed by extraction in Muspratt solution resulted in significant losses of active material by complexation with hydrazine.

This need not have been an obstacle to the development of an acceptable method but the procedure defined below is considered to be more effective and straightforward. Since this work was carried out, a method of positive plate analysis using acetic acid in the presence of hydrazine has been published,[27] but it does require that the electrode be crushed and the metallic nickel be removed magnetically prior to dissolution (see further discussion later).

In the case of sodium borohydride, it was found that spontaneous decomposition occurred and that the extraction process was complicated by side reactions with the decomposition products.

The second modification of the basic method to counteract the effect of the presence of electroreducible species involved potentiostatting the positive plate at a low positive potential during the extraction process. The first step in defining this technique was to establish the potential range in which no nickel dissolution could occur. A current potential scan was carried out on a pure nickel plaque in Muspratt solution containing divalent nickel.

The 5-cm^2 plaque was first held at 0.0 V versus the reversible hydrogen electrode (RHE) while N_2 was bubbled through the solution. The initial cathodic current corresponding to reduction of dissolved O_2 decayed to less than 0.1 mA/cm^2 in a matter of minutes. This small cathodic current was maintained up to a potential of ~ +100 mV versus RHE when the current became anodic. The anodic current then increased until, at +300 mV versus RHE, it reached a value of 5 mA/cm^2. This value subsequently decreased for further increase in potential but remained significant at ~ 1 mA/cm^2 (see Fig. 1). From this behavior, we may deduce that the passive film normally formed on nickel at potential between 200 and 300 mV versus RHE is not stable in Muspratt solution. However, below +100 mV versus RHE, no dissolution of nickel takes place. We considered the possibilities that: (1) as the concentration of nickel increased during the extraction process, nickel might be electrodeposited from solution, and (2) further reduction of the discharged active material to metallic nickel could also occur. With regard to the latter point, Kronenberg[29] has reported that reduction of $Ni(OH)_2$ does not take place until the H_2 evolution potential is reached. In practice, we have found that, at +25 mV versus RHE, we observed a cathodic current of between 2 and 4 mA for a 5-cm^2 plate. This current was most probably due to oxygen reduction, but even if it corresponded to nickel deposition (from either process listed above) it would result in only 10 mg weight increase in the normal extraction time of 5 hr, i.e., less than a 1% error in the extraction of a 5-cm^2 plaque that weighed approximately 1 g.

With the opportunity to ensure complete extraction of active material without the risk of corrosion of the substrate, it is possible to determine with a reasonable degree of accuracy the crystalline water content of the active material. The significance of the water content in terms of utilization and charge acceptance will be discussed in detail in the future. At this time, it is sufficient to note that this is an important aspect of positive plate analysis. Water content is determined by comparing the weight loss on extraction with the total nickel content of the extraction solution determined by dimethyl glyoxime. The procedure, for a plate of known weight and approximately 5 cm^2 in area, is immersion in 175 ml of Muspratt solution at 70 °C in a four-necked flask under a potential control (Fig. 2). A dynamic hydrogen reference electrode,[30] set up behind a glass frit, was used to establish the positive plate at a potential of 25 mV versus RHE. The counterelectrode of Pt, also behind a frit, was inserted in the third neck of the flask. Nitrogen was bubbled through the solution to minimize the effect of the oxygen evolved at the counterelectrode on the extraction process. The extraction solution took on a distinct blue color within 20 to 30 min and was routinely replaced with fresh solution after 1 hr. The extraction

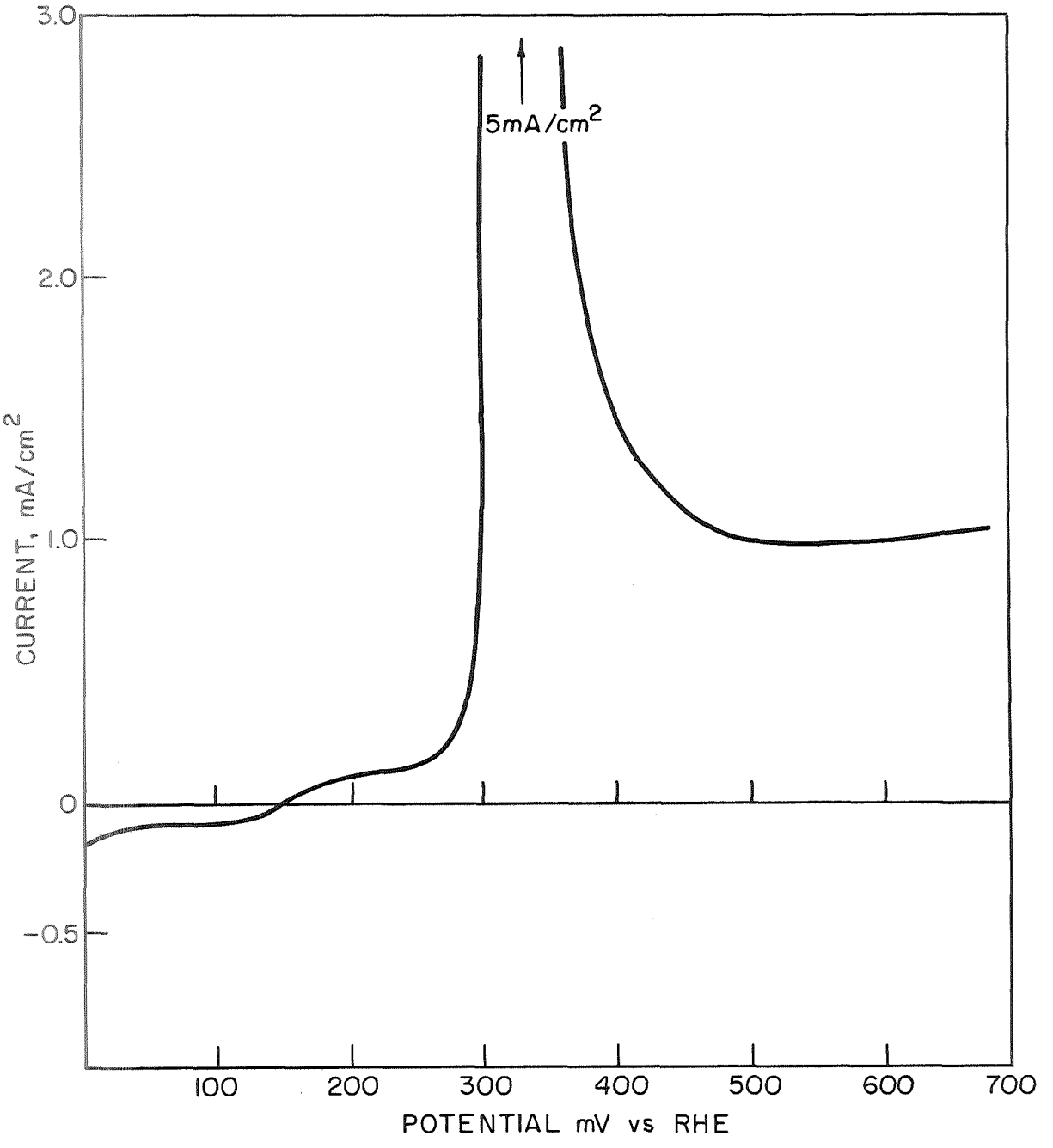

Fig. 1. Current voltage curve for nickel plaque in Muspratt solution

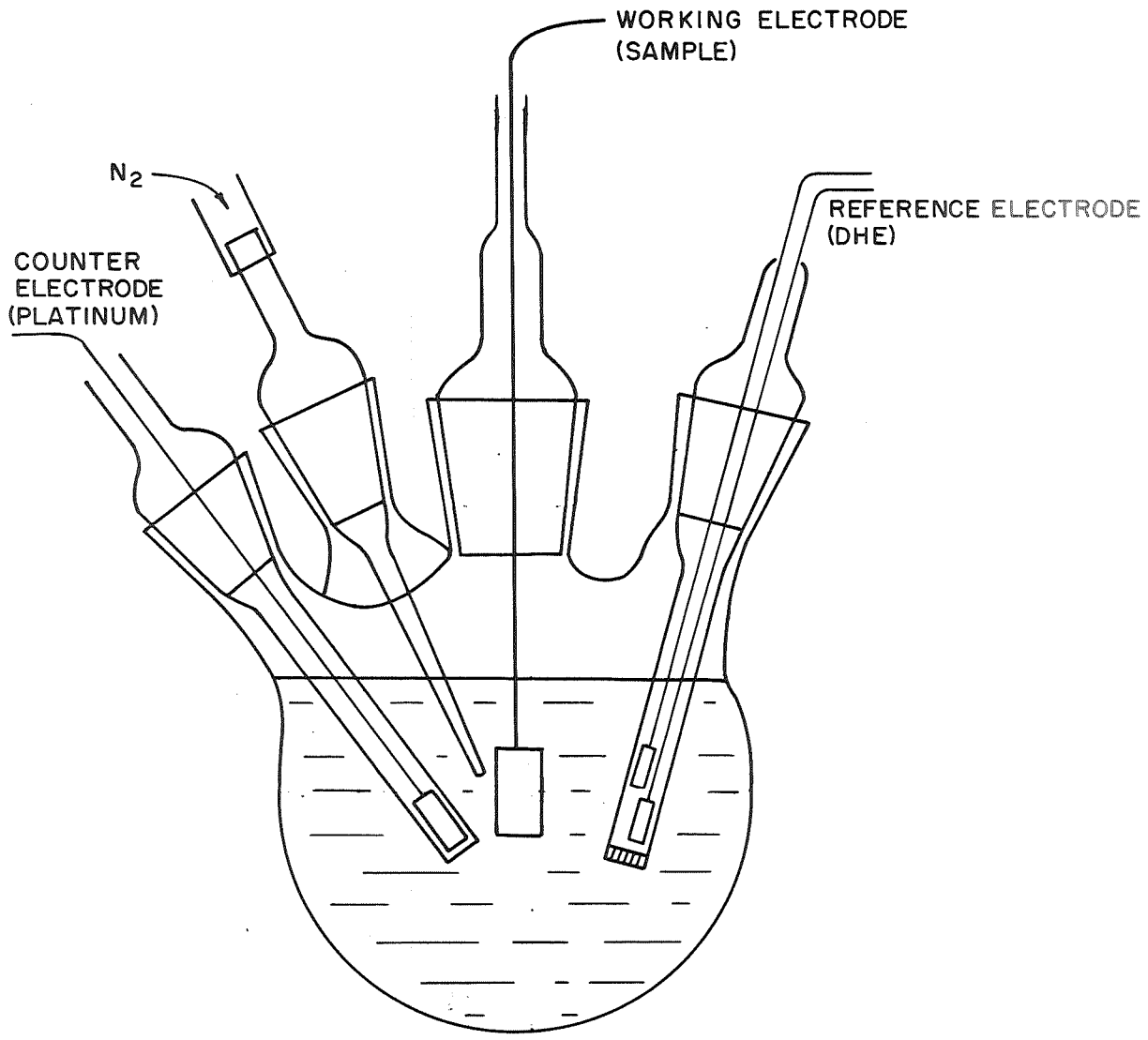

Fig. 2. Extraction of active material from positive plate under potential current

process was continued for 4 hr or longer if the blue coloration persisted. The nickel content of the combined extraction solutions was determined by precipitation with dimethyl glyoxime. The plaque after extraction was carefully washed, dried, and weighed to determine the total weight loss. Comparison of the weight/unit area after extraction with the weight/unit area of the plaque prior to impregnation gives a measure of the extent of plaque corrosion that took place during impregnation or cycling. As defined above, the water content of the active material is calculated from the weight of active material extracted and the nickel content as determined by dimethyl glyoxime. For $Ni(OH)_2 \cdot 1.5\ H_2O$ stoichiometry [$\alpha\ Ni(OH)_2$], the water content would be 22.6%, for $Ni(OH)_2 \cdot H_2O$ 16.8% and for $Ni(OH)_2 \cdot 0.5\ H_2O$ approximately 9%. Details of the experimental procedure are set out in Appendix II.

In Table IV, some of the more interesting results are set out. Samples 1a and 1b were adjacent pieces cut from the same plate; sample 1a was examined without control, for 1b the potential was maintained at 25 mV versus RHE. The results indicate that in the case of the green plate (i.e., prior to formation and cycling) there is not too great a problem in analyzing for active material content and that potential control is not essential (as long as air is carefully excluded). Very good agreement was obtained for the two determinations; it is interesting to note that the plaque weight after extraction is some 5% lower than the plaque weight prior to impregnation. Since these plates were not cycled, this weight loss must represent the extent of corrosion of the plaque during the impregnation process.

In contrast, samples 2a and 2b demonstrate the requirement for potential control once the plate has been formed or cycled. The percentage weight loss of sample 2a is some 2.5% greater than 2b. This can only be attributed to plaque corrosion since these are adjacent samples from a plate of uniform weight distribution. The extent of corrosion is also reflected in an apparent increase in the percentage $Ni(OH)_2$ in the plate as calculated from the Ni^{2+} content of the extraction solution. For sample 2b extracted under potential control, the plaque weight after extraction was almost identical to that of the plaque prior to impregnation. Note that both the plates used for samples 2 and 3 were prepared by impregnation method that did not use nitric acid in the impregnation solution, so that little corrosion of the plaque would be expected. Samples 3a and 3b demonstrate the degree of improvement in the analysis of a discharged plate when the active material is extracted under potential control. In this case, there is excellent agreement in the determination of Ni content in the active material. The slightly greater weight loss observed for 3b can probably be attributed to an increased water content in the active material that was cycled. Samples 1 through 3 were listed to make the specific points above. Samples 4 and 5 are typical examples of results obtained routinely. Note that despite good agreement for the weight per unit area of these plates and the uniform weight loss, the actual Ni^{2+} content of the active material is significantly different. Some corrosion of these plaques is evident during impregnation.

It is apparent from the data presented in Table IV that the determination of the water content from the difference between weight loss and direct determination of Ni^{2+} cannot have a

Table IV. Analysis of Positive Plates

Sample	Comments	Potential Control During Extraction*	Plate Wt Before Extraction, g/cm^2	Plaque Wt, g/cm^2 After Extraction	Plaque Wt, g/cm^2 Before Impregnation	% Wt Loss on Extraction	% $Ni(OH)_2$ by Analysis	% H_2O in Active Material
1a	Green plate	No	0.2309	0.1931	0.2036	16.4	15.0	9
1b	Green plate	Yes	0.2300	0.1907	0.2036	17.0	15.0	13
2a	Cycled plate in discharged state†	No	0.2067	0.1670	0.1750	19.2	19.2	—
2b	Green plate†	Yes	0.2133	0.1769	0.1750	16.8	17.2	—
3a	Green plate†	Yes	0.2530	0.2046	0.2036	19.1	19.3	—
3b	Cycled plate in discharged state†	Yes	0.2503	0.2004	0.2036	19.9	19.3	(3)
4	Green plate	Yes	0.2448	0.1922	0.2027	21.7	21.6	—
5	Cycled plate in discharged state	Yes	0.2464	0.1915	0.2027	22.3	18.7	15

* Extraction in Muspratt solution at 70 °C, potential control at 25 mV versus RHE.

† Plates impregnated by Fleischer method without nitric acid in impregnation solution.

high degree of accuracy since it is derived as a small difference between two relatively large numbers. However, the figures presented are not considered typical since no special precautions were taken to ensure reproducible drying conditions from sample to sample. Furthermore, for cycled plates, it is necessary to define the K^+ content of the active material since this will also contribute to the weight loss and would be a source of error in the determination of water content. In principle, therefore, it is possible to determine the water content of the positive active material though no concrete examples of the technique are presented here since our prime interest in this program is just to determine Ni^{2+}.

In more general terms, the conclusions we may draw are that this technique of extraction of positive active material under potential control provides a quantitative method for the determination of:

1. The amount of active material in a positive plate
2. The atom % Ni^{2+} in the active material
3. The extent of plaque corrosion, both in impregnation and on cycling.

The one limitation is that analysis under potential control can only be carried out with plate in its lowest possible state of charge.

D. Determination of State of Charge of the Positive Plate

A capability to determine the quantity of active material in a positive plate as described above is useful in assessing the uniformity of an impregnation process. It does not, however, provide enough information to calculate the utilization of the active material since the stoichiometry of the charged state is nonintegral (as is the discharged state after cycling). Since both the stoichiometry and the distribution of the active material could be functions of the impregnation process and conditions, it is desirable to be able to define which impregnation process and which conditions give rise to the most uniform and predictable behavior, i.e., a method of determining the state of charge is required. For reasons that will become apparent, rigorous definition of the state of charge is probably not attainable; the problem again is one of an error caused by corrosion of the substrate. However, this error can be minimized if certain experimental precautions are taken. Then, if it is assumed that this systematic error is a relatively consistent one, a useful analytical method is avialable for comparative purposes.

The state of charge is commonly defined in terms of its active oxygen [O] equivalent. The standard method of determining active oxygen is to liberate iodine from a slightly acid solution of potassium iodide, then to titrate the free iodine (present as I_3^-) against a standard solution of sodium thiosulphate.

In the following, we will present the problems that occur in practice when this method is attempted and also discuss the precautions that can be taken to alleviate them. In the initial experiments, the procedure started with washing and drying the plate, followed by immersion in 25 ml of a sodium acetate buffer at pH 4.5 (20 g sodium acetate and 15 ml of glacial acetic acid made up to 200 ml) containing 5 ml of 25 wt % Kl solution. The flask was then sealed and

left overnight. The free iodine was titrated against 0.05N sodium thiosulphate using starch as an indicator at the end point. Typical results are listed in Table V. Note that separate determination of the $Ni(OH)_2$ content of the plate by the method described above is necessary. The procedure adopted was to use a 10-cm^2 sample of plate and use approximately half the sample for the $Ni(OH)_2$ determination and half for active [O] measurement (uniform distribution is assumed for this size of sample). The apparent nickel valence was calculated from the mole ratio of [O] to $Ni(OH)_2$ assuming an equivalent weight of 8 for [O].

Table V. Preliminary Determinations of State of Charge

Sample	Wt/unit Area, g/cm^2	Wt % $Ni(OH)_2$	Wt %[O] in Active Material	Apparent Ni Valance*
Green plate	0.2113	17.2	0.39	2.04
Charged state	0.2067	19.2	3.38	2.39
Charged state	0.2055	14.0	3.56	2.42

*Calculated from nickel valence $= 2 + \frac{2 \text{ mol [O]}}{\text{mol } Ni(OH)_2}$.

It is immediately obvious that the apparent nickel valence in the charged state determined by the method detailed above is too low. Capacity measurements assuming 1F/mol $Ni(OH)_2$ and 100% utilization indicated that the valence should be in excess of 3. (It should also be noted that the three samples listed in Table V were not in any way related and were not intended to be a test of reproducibility.)

Several effects were examined at this time to try to explain the low values. These included:

1. The extent of overcharge
2. KOH concentration
3. The number of cycles
4. Time of reaction between charged plate and KI.

These results will not be included since the values obtained showed little improvement. However, the trends observed did help to define improved analytical procedures. The active oxygen content in contrast to the results reported by Aia[21] did not show an increase with the extent of overcharge. Plates charged to 100%, 200%, and 300% exhibited random behavior giving rise to apparent Ni valancies of between 2.4 and 2.5. Increasing the concentration of KOH during the charging process from 25 to 30% showed an increase in active oxygen content of approximately 20%.

These two factors pointed to the serious source of error associated with self discharge in the washing and drying process, particularly during the washing. There was also an apparent increase in active oxygen content on cycling even though the measured discharge capacities

were approximately constant. It is now considered that this is an artifact of the analytical procedure, possibly related to self-discharge rates, which could vary significantly in the first few cycles.

Interesting information was also obtained in the examination of the effect of contact time between the charged positive plate and the acidified KI. The pattern of the results is shown in Fig. 3. The apparent active oxygen content increases with time up to 6 hr. It then decreases at a somewhat slower rate in an approximately linear fashion. Note that there is a significant decrease in [O] between the maximum figure at 6 hr (overnight) routinely used in the procedure discussed above. (The values are still low in comparison to the discharge data, because these plates were washed and dried before analysis.) The lower value obtained for the active oxygen content after long reaction times is considered to be due to the reduction of I_3^- by metallic nickel. The charged plate is at a potential where the metallic nickel substrate would normally be protected by a passive layer of nickel oxide. However, in the presence of acetate ions which can complex Ni^{2+} or even possibly potassium iodide, this passive film is attacked and nickel dissolution can occur. The accompanying cathodic process could be either discharge of active material or reduction of I_3^-. From the experimental behavior depicted in Fig. 1, the latter reaction must occur; it is also possible that the former reaction also occurs. The extent to which the active material is discharged is the systematic error referred to in the preliminary discussion beginning this section. It will be considered in more detail below.

As a result of the evidence presented above, two modifications were introduced in the analytical procedure. The first was the elimination of the washing and drying step. Plates were transferred immediately on completion of the charge or overcharge process into the iodide solution, i.e., self discharge on dilution and spontaneous self discharge on open circuit in KOH were kept to a minimum. In contrast to the washing process in which bubbles of oxygen are formed quite rapidly, immersion in the iodide solution did not result in gassing.

The second improvement in the basic technique follows a recommendation of Harivel.[26] Accumulation of I_3^- in solution during the reaction with the positive plate is prevented by regular addition of sodium thiosulphate. As soon as the solution change from colorless to the pale straw color associated with free iodine is apparent, a known small volume of thiosulphate is added. This procedure is followed until the reaction is complete. For a 1-g sample, the total reaction time is 6 to 7 hr. The end point for the thiosulphate titration was determined in the presence of starch. Note that in the latter part of the reaction it is important not to add too much thiosulphate.

In practice, the first improvement in the elimination of washing and drying was put into effect before the latter. The results shown in Table VI show the marked effect of this change. The values for the active oxygen content are, however, still considered to be low because of the very long contact times with the iodide.

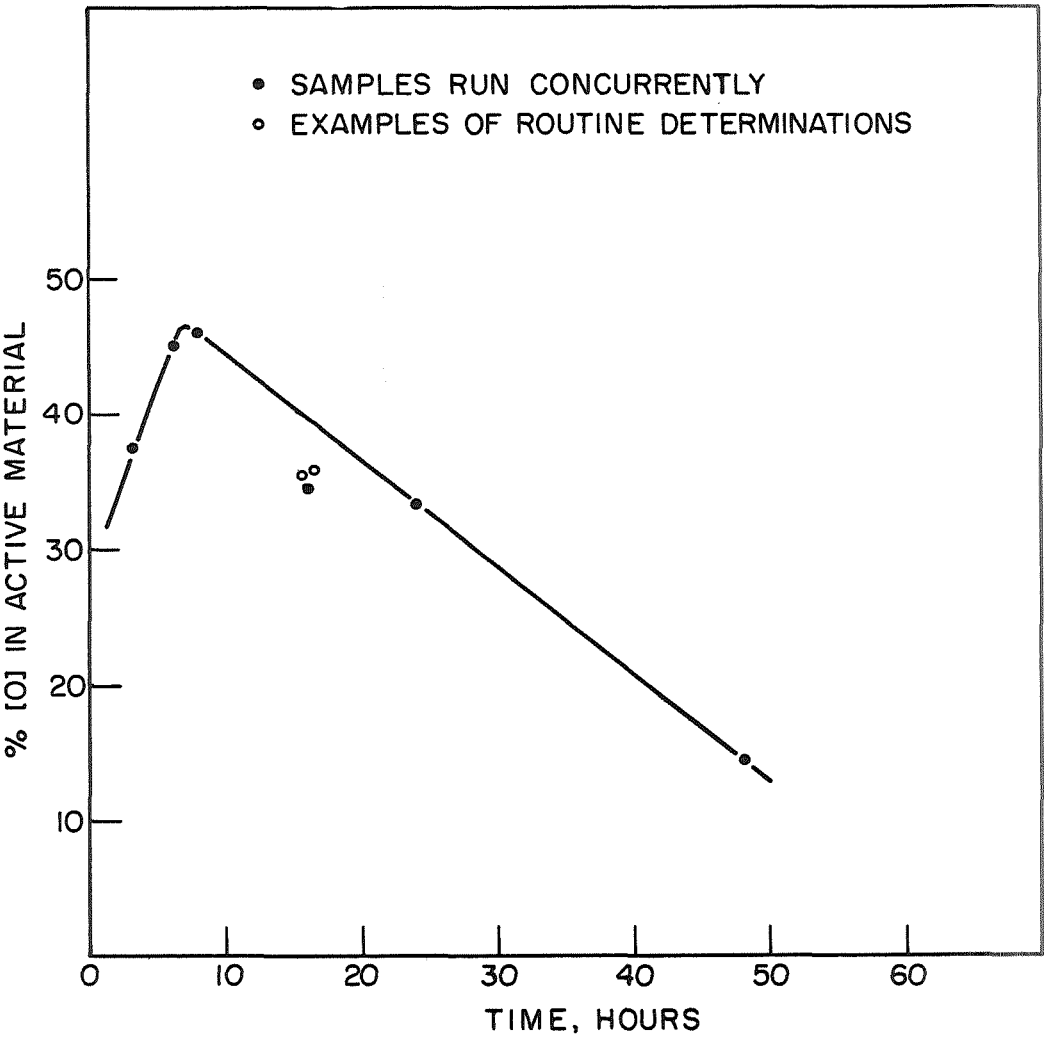

Fig. 3. Variation of apparent active oxygen content as a function of contact time with acidified KI

Table VI. Effect of Washing and Drying of Sample on Active [O] Determination

Sample	Weight Per Unit Area, g/cm^2	Wt % $Ni(OH)_2$	Wt % [O] in Active Material*	
			Washed and Dried	Direct Transfer
1	0.2503	19.1	4.35 (2.50)	6.97 (2.80)
2	0.2008	13.1	4.36 (2.50)	8.27 (2.95)

*Figures in parenthesis are corresponding apparent nickel valencies.

When the second improvement was put into effect, the measured values for the active oxygen content showed a further increase to nearly 10% by weight of the active material. The revised procedure was then to transfer the plate, on termination of the charge or overcharge process, directly into the iodide solution and to add 5 ml of 0.025N sodium thiosulphate each time the color of free iodine was apparent in the solution. Initially, these additions were made at approximately 15-min intervals, but lengthened considerably as the reaction proceeded. Some typical results obtained by this method are presented in Table VII.

The first point to establish from the results is that reasonable reproducibility is achieved with this technique. See for example samples 5, 6, and 7. However, in comparison with measured capacities, the values obtained for the apparent nickel valence are too low. Consider for example sample 5. This sample contained 0.134 g of active material, determined as $Ni(OH)_2$ on an adjacent piece of the plate in the discharged condition. We may then calculate a theoretical capacity based on the apparent nickel valence of 3.0 in the charged state and 2.2 in the discharged state (from the figures of Table VII). This value is 0.031 Ahr. Since the measured capacity to a 1.0 V cutoff was 0.0385 Ahr, the analytical determination of the valence of the charged state must still be too low.

The results otherwise show a high degree of internal consistency. The apparent valence increases with the extent of overcharge. The charging process up to 50%* is demonstrated to be much more efficient than the latter stages. The same apparent nickel valence is observed for the 100% charge and 150% charge. This probably reflects a greater attack on the nickel substrate for the more highly charged plate. The small loss in capacity generally observed on open circuit stand is confirmed by a smaller active oxygen content for sample 4, compared to samples 5, 6, and 7.

The somewhat high values of the valence in the discharged state to a 1V cutoff can probably be attributed to incomplete discharge at the relatively rapid C/2 discharge rates used in these experiments. Overdischarge for 15 min results in a more acceptable value.

In view of the fact that the active oxygen determination in the charged state is still low,

* Based on discharge capacity observed in previous cycle after 100% overcharge.

Table VII. Apparent Ni Valence as Function of Charge, Overcharge, and Overdischarge

Charged State

Sample	% Charge at C/2 Rate	Wt % [O] in Active Material	Apparent Ni Valence
1	50	6.0	2.69
2	100	7.5	2.87
3	150	7.5	2.87
4	200*	8.25	2.96
5	200	8.95	3.04
6	200	9.25	3.07
7	200	9.35	3.08
8	1000	9.75	3.13

Discharged State

Sample	Time of Over-discharge, Min	Wt % [O] in Active Material	Apparent Ni Valence
9	0	3.2	2.37
10	5	2.7	2.31
11	15	1.8	2.21

*20 min stand at open circuit prior to analysis.

it is difficult to define active material utilization precisely. The active oxygen content of the discharged state gives some measure of material not cycling, but there are no means to determine whether any divalent nickel is present in a fully charged plate.

As a footnote, it might be added that attempts were made to follow weight changes in the positive plate during charge and discharge cycles, the objective of determining the extent of hydration of the charged active material. (A separate determination of K^+ content was envisaged.) The results obtained using a Cahn electrobalance showed considerable hysteresis and very complex oscillatory phenomena in relatively small changes in weight. Time did not permit rigorous pursuit of this behavior.

III. IMPREGNATION METHODS

A. Introduction

The aim of this study of impregnation methods was to define a systematic procedure to produce uniform plates for nickel cadmium cells.

The basic methods were outlined in the first section of this report. The prime variables considered for each method were loading and the morphology of the active material. The plates were assessed in terms of the reproducibility and uniformity of weight gain/unit area, capacity and utilization, and the extent of plaque corrosion.

B. Experimental Program

The experimental program set up to study the influence of loading and morphology in uniformity and reproducibility of plate characteristics consisted of the following:

Fleischer Method

Positives (PF series)	saturated $Ni(NO_3)_2$ + nitric acid, 25% KOH at 80° C
	– 2, 5, 8, and 12 impregnation cycles, cathodized at 150 mA/cm^2
	– 2, 5, 8, and 12 impregnation cycles, cathodized at 300 mA/cm^2
Negatives (NF series)	saturated $Cd(NO_3)_2$ + nitric acid, 25% KOH at 80° C
	– 2, 5, 8, and 12 impregnation cycles, cathodized at 150 mA/cm^2
	– 2, 5, 8, and 12 impregnation cycles, cathodized at 300 mA/cm^2

Chemical Conversion

Positives (PC series)

saturated $Ni(NO_3)_2$ + nitric acid, 25% KOH at 80° C

– 2, 5, 8, and 12 impregnation cycles

50% saturated $Ni(NO_3)_2$ + nitric acid, 10% KOH at 80° C

– 2, 5, 8, and 12 impregnation cycles

Negatives (NC series)

saturated $Cd(NO_3)_2$ + nitric acid, 25% KOH at 80° C

– 2, 5, 8, and 12 impregnation cycles

50% saturated $Cd(NO_3)_2$ + nitric acid, 10% KOH at 80° C

– 2, 5, 8, and 12 impregnation cycles

Modified Fleischer Method

Positives (PCF series)

saturated $Ni(NO_3)_2$ + nitric acid, 25% KOH at 80° C

– 2, 5, and 8 impregnation cycles, dried at 80° C, cathodized at 150 mA/cm^2.

Electrochemical Method

Positives (PE series)

4M $Ni(NO_3)_2$ solution, 25° C

– cathodized at 0.34A for 5, 10 and 20 min

2M $Ni(NO_3)_2$ solution, 25° C.

– cathodized at 0.34A/cm^2, 0.42A/cm^2 and 0.68A/cm^2 for 5, 10, and 20 min.

Negatives (PN series)

saturated $Cd(NO_3)_2$ solution, 25° C

– cathodized at 0.05 A/cm^2 for 10, 20, 30 and 60 min

– cathodized at 0.10 A/cm^2, 0.15 A/cm^2 for 5, 10, and 20 min.

The objectives of the program were to define the uniformity and reproducibility of:

1. Weight gain/unit area
2. Capacity and utilization of active materials on cycling
3. The extent of plaque corrosion

as a function of the preparative conditions and loading of the active material. The preparative conditions are considered to control the morphology of the active material which in turn will affect utilization. The loading with active materials and their distribution in the porous mass are also obvious factors to consider in defining utilization.

C. Impregnation Procedures

The basic methods of plaque impregnation have been described previously but will be repeated here for completeness.

1. Fleischer process

The equipment used for the impregnation process is shown in Fig. 4. It consists of an impregnation tank and reservoir for the impregnation solution. The vacuum lines permit the transfer of the impregnation solution to and from the impregnation tank. The plaques were mounted on a terminal post at the commencement of the process and inserted in the impregnation tank. The jar was evacuated for 5 min before the impregnation solution was drawn in. The tank was then opened to atmospheric pressure. After a 5-min soak period, the plaque was transferred directly into the KOH solution at 80 °C. The terminal post was inserted into a sleeve in the lid of the KOH bath and the necessary cell connections made before immersion so that the cathodic current flows immediately on immersion. The effect of this current is to reduce NO_3^- ions in the plaque structure ensuring more complete conversion and localizing the deposition within the plaque structure. The KOH solution was open to the atmosphere only during the immersion of the electrode. At all other times, the surface of the solution was blanketed with N_2 to prevent carbonate buildup. After immersion in KOH for 20 min, the plaque was removed into a beaker of distilled water. Subsequently, the plates were thoroughly washed by forcing distilled water through the plaque until the wash water in contact with the plate had a pH less than 8.0. No loss of active material was observed in this process, but if any losses did occur, we may assume that it was loosely adherent material that might not cycle efficiently. The plate was then dried and weighed and the whole process repeated. The basic conditions for this process were near-saturated nickel nitrate, 1534.6 g $Ni(OH_3)_2 \cdot 6\,H_2O$ dissolved in 465.4 ml water with 4 ml of 70% nitric acid, 25% KOH at 80 °C, with a cathodization current of 150 mA/cm^2.

For negative plates, the basic solution was made up from 1456 g of $Cd(NO_3)_2 \cdot 4\,H_2O$ in 544 ml of water with 4 ml of 70% nitric acid. All other conditions were identical to those of the positive.

2. Chemical conversion

The chemical conversion of the nitrates to the hydroxides was carried out in almost identical fashion to the Fleischer process. The main difference was that, after vacuum impregnation with the nitrates, the plaques were dried for 2 to 3 hr at 80 °C. They were then immersed in KOH at 80 °C without cathodization. Solution compositions were as defined for the Fleischer process.

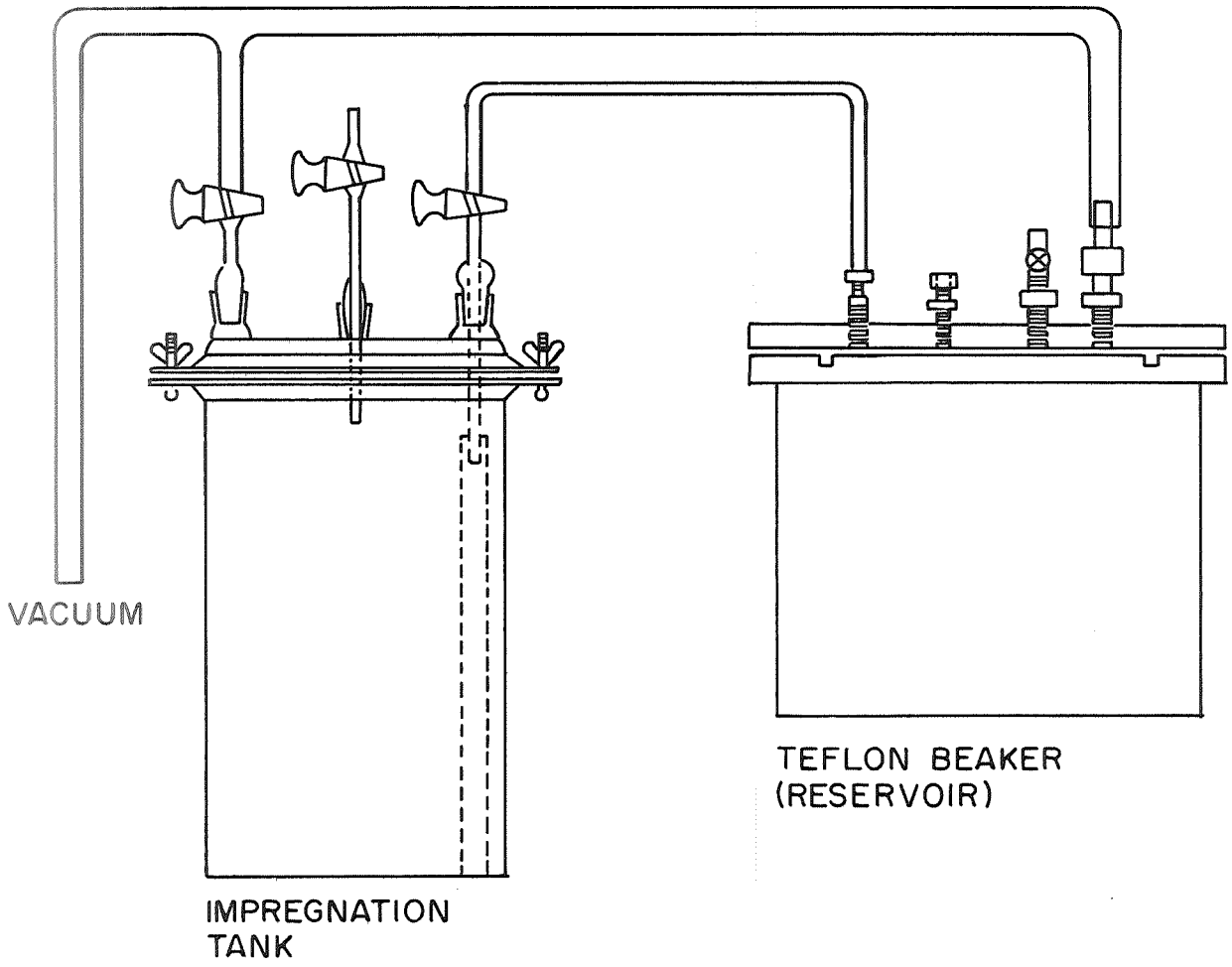

Fig. 4. Vacuum impregnation apparatus

3. Modified Fleischer approach

A limited number of preparations were carried out in which the drying step of the chemical conversion approach was included in the Fleischer Method. The drying conditions were 2 to 3 hr at 80° C.

4. Electrochemical conversion

For electrochemical conversion, the plaque to be impregnated was mounted in a Teflon jig with two symmetrically disposed counterelectrodes of platinum gauze. The jig was immersed in either nickel or cadmium nitrate, thermostatted at 25° C. Current was then passed through the cell with the plaque as cathode.

D. Plate Characterization

1. Weight distribution of active materials

The 5 × 2 1/2-in. plates were cut into three pieces of approximately equal size 1 2/3 × 2 1/2 in. The areas were determined by projection onto squared paper, and the weight of each piece of plate measured. In the following presentation of the results, the pieces are labelled A, B, and C; with the top piece, i.e., the nearest to the current collecting tab in the Fleischer process, being piece A.

2. Capacity measurements

Capacity measurements were made on a section of piece A, approximately 1 1/2 × 1 1/2 in., the remainder of the piece being used for chemical analysis in the green state. Capacities were determined in flooded cells with oversize counter electrodes. Both charge and discharge were carried out at the C/2 rate* (i.e., a rate at which the plate would be discharged in two hours). To prevent overdischarge, particularly of the negative plates, discharge was carried out to a 1 V cutoff. Each plate received 100% overcharge based on the C/2 rate. The plates were cycled until three consecutive cycles gave concordant values. This was usually achieved within six cycles for the positives and six to eight cycles for the negatives.

3. Chemical analysis

The procedures for chemical analysis are defined in the previous section. The negative plates prepared by the Fleischer method were examined in the green state (prior to cycling) to determine the relative quantities of cadmium and cadmium hydroxide. (Cadmium is produced from cadmium hydroxide in the impregnation process during cathodization though the conversion is not complete.) This determination is essential to define the total quantity of cadmium in the plate in order to calculate the utilization of the active material on cycling.

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* The rate selected in practice was defined as the C/2 rate based on weight gain. This does mean different current densities for widely different loadings.

The positive plates were analyzed in the green state and in the discharged state after cycling, for the quantity of active material, its water content, and the extent of plaque corrosion.

BET surface areas were measured using an Engelhard Isorpta for selected positive plates.

E. Experimental Data

The plate preparations carried out are defined on pages 25 and 26. The code letters used are as follows:

P - Positive
N - Negative
F - Fleischer method
C - Chemical conversion
E - Electrochemical conversion

The letters a and b are used to denote the duplicate preparations made in each case. Thus, the code PC1a represents the first preparation of a positive plate by chemical conversion according to the details set out in the data sheet. PC1b represents the duplicate preparation. The modified Fleischer approach for the preparation of positive plates, in which the drying step of the chemical conversion process is included, is denoted as PCF.

IV. DISCUSSION

A. Fleischer Method - Positive Plates

A summary of the positive plate impregnation data by the Fleischer method is given in Table VIII. Comprehensive data sheets on each impregnation were presented in an Appendix to the Seventh Quarterly Report. Plates were prepared in duplicate with 2, 5, 8 and 12 impregnations. The first series PF1 through PF4 was cathodized at 150 mA/cm^2, the second PF5 through PF8 at 300 mA/cm^2. Considering the weight gain first, reproducibility from preparation was reasonable. Little distinction can be made from these data between the reproducibility of 150 mA/cm^2 and at 300 mA/cm^2. In general, there is better reproducibility for the A pieces (i.e., closest to the point of current takeoff). In addition to the final weight gains listed, we may also assess reproducibility by comparing the weight gains for the whole plate at the end of each impregnation cycle for each plate preparation, e.g., we may compare the first five impregnations of PF3 with the five impregnations of PF2. The data for PF1 through PF4 are presented in Fig. 5. The abscissae are offset to permit separate identification of the curves. Good reproducibility is indicated by a horizontal line through equivalent points of the different curves. It is apparent that very good reproducibility is obtained in the first four cycles, that we begin to see some deviation at the fifth cycle, and that quite considerable variation is observed for a greater number of cycles. However, for those plates cathodized at 300 mA/cm^2, much better reproducibility is observed for the larger number of impregnations (Fig. 6).

The theoretical capacities listed in Table VIII were derived from the amount of active material present in the plates, determined as $Ni(OH)_2$ by chemical analysis. Since the water content of the active material is found to vary from preparation to preparation (as discussed previously), these theoretical capacities for plates PF1 through PF4 show an anomaly in that the value for PF4 is less than that of PF3. It would appear that the preparative conditions for PF4 were different from the rest of the series. This factor was also apparent in the analysis of reproducibility. The same trend was noted in the measured capacities. The capacity of PF3 of 0.35 Ahr/cm^3 is typical of that for plates used in battery manufacture. The number of cycles to achieve this capacity, however, is greater than that normally required in commercial practice probably because the extent of plaque corrosion (the corrosion product becomes positive active material) is a lot less in the preparations considered here. This is because of the rapid handling of the plates and thus minimum contact time with the nitric acid. The utilization

Table VIII. Capacity, Weight-Gain and Utilization – Fleischer Method, Positive Plates

	Impregnations	Active Material, g/cm^2 A	B	C	Capacity, Ahr/cm^3 Theoretical*	Measured†	Utilization, %
150 mA/cm^2							
PF1a	2	0.0353	0.0348	0.0306	0.163	0.111	68
b		0.0351	0.0350	0.0331			
PF2a	5	0.0709	0.0696	0.0640	0.247	0.199	81
b		0.0680	0.0660	0.0672			
PF3a	8	0.0889	0.0956	0.0871	0.312	0.347	110
b		0.0887	0.0927	0.0823		0.330	
PF4a	12	0.0921	0.0885	0.0913	0.281	0.315	112
b		0.0919	0.0951	0.0968		0.315	
300 mA/cm^2							
PF5a	2	0.0351	0.0358	0.0309	0.119	0.111	94
b		0.0308	0.0307	0.0289			
PF6a	5	0.0671	0.0728	0.0672	0.248	0.221	86
b		0.0714	0.0643	0.0635		0.241	
PF7a	8	0.0923	0.0928	0.0909	0.326	0.298	91
b		0.0936	0.0927	0.0936			
PF8a	12	0.1129	0.1035	0.1111	0.398	0.347	87
b		0.1088	0.1145	0.1112			

*Based on chemical analysis for $Ni(OH)_2$ and a 1e charge discharge process.

†Measured on piece A.

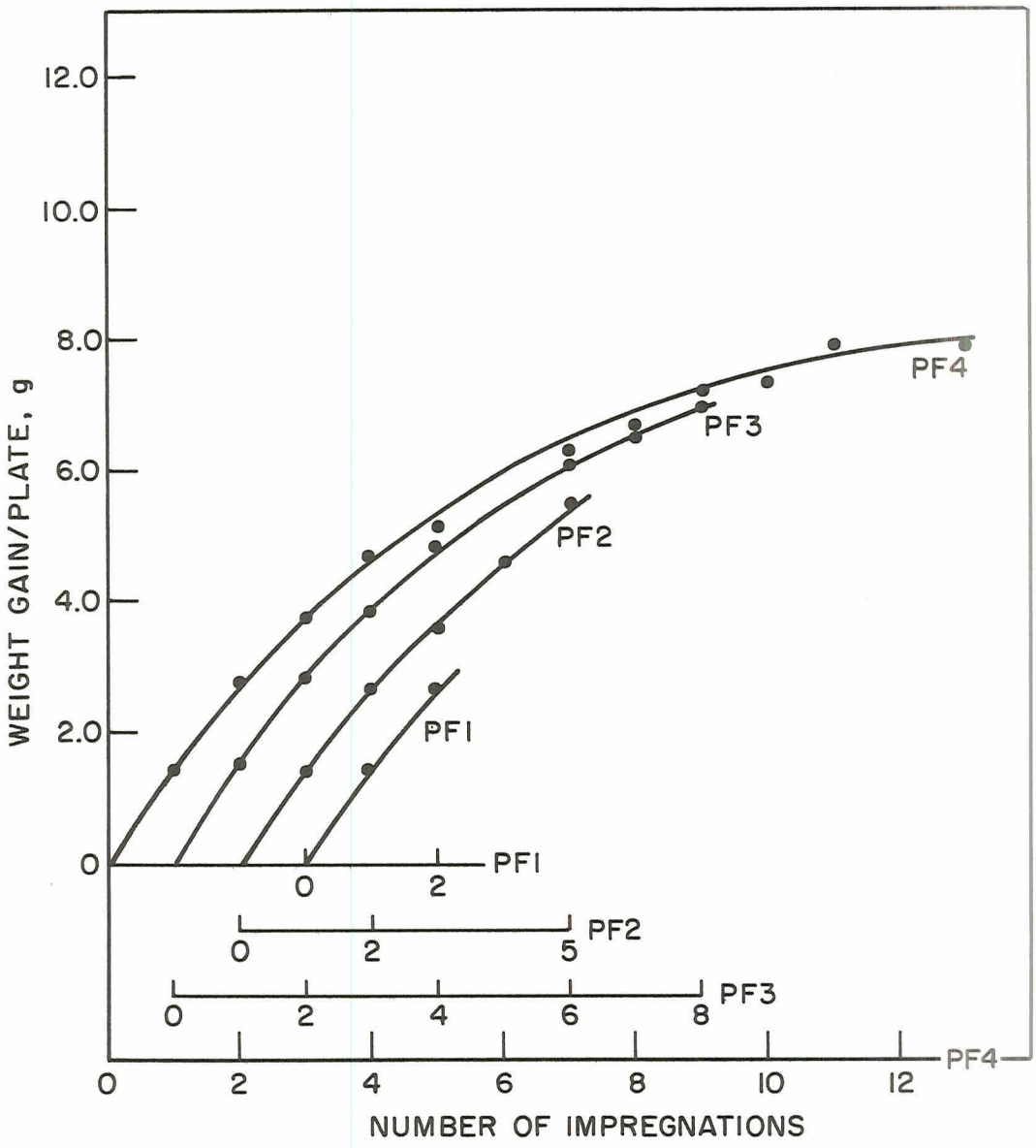

Fig. 5. Reproducibility of Fleischer impregnation process – positive plates cathodized at 150 mA/cm^2

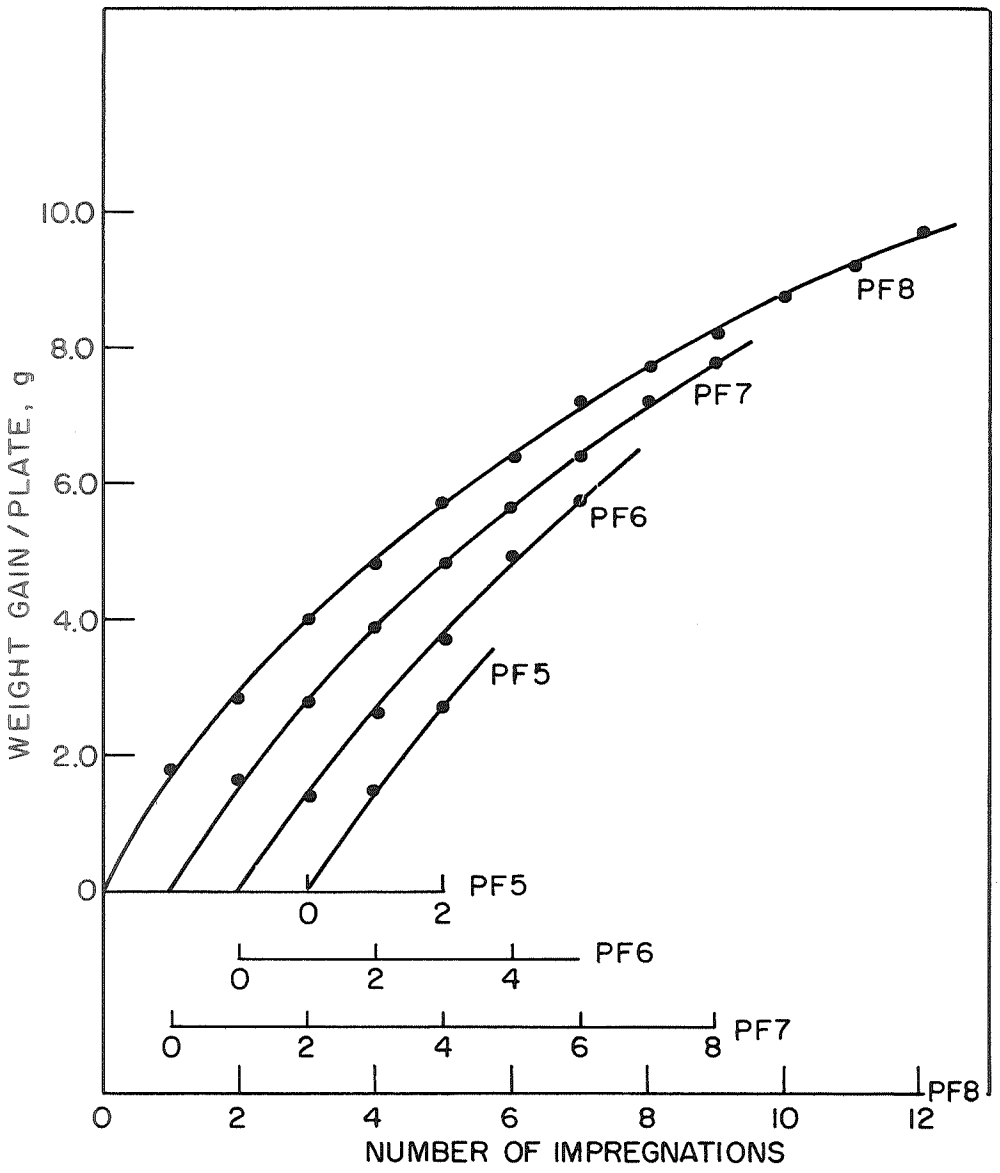

Fig. 6. Reproducibility of Fleischer impregnation process – positive plates cathodized at 300 mA/cm^3

figures are somewhat surprising. Instead of showing a decrease with increasing loading, the values are more or less independent of loading for the plates cathodized at 300 mA/cm^2. For the plates cathodized at 150 mA/cm^2, utilization increases with loading.

B. Chemical Conversion - Positive Plates

The data collected for positive plates prepared by chemical conversion are presented in Table IX. Reproducibility of weight gain between the duplicate preparations was slightly better than the plates prepared by the Fleischer method. In comparing the weight gain per impregnation cycle (Figs. 7 and 8), it may be noted that the plates prepared with the less concentrated impregnation solutions showed much better reproducibility. For the saturated impregnation solution, plate PC3 shows quite different characteristics from the rest of the group. The scatter in the remainder is slightly greater than that observed in the Fleischer process.

Uniformity of weight gain in a particular plate for the chemical conversion process proved to be better than that of the Fleischer method. No pattern in weight distribution could be observed, and the uniformity improved with increasing number of impregnation cycles. For the most part, the spread in distribution was within 4%. In the better examples, the deviation from the mean value is less than ± 1%.

Theoretical capacities were based on chemical analysis of the plates. For these plates, the pattern of capacity and weight gain did not show the anomalies observed for the Fleischer process. Measured capacities were quite reproducible for the replicate plates. For the same number of impregnations, the capacities were higher than the comparable number for the Fleischer process with saturation solution. This is due to the greater corrosion of the plaque that probably takes place during the drying of the plate after impregnation with the nickel nitrate-nitric acid solution. This fact was confirmed by the chemical analysis and is discussed in more detail later.

Utilization of the active materials is again independent of loading, though it is somewhat lower for PC4. Note that utilization figures can be greater than 100% since they are based on a 1-electron transfer per Ni atom in the active material. Since the charged state is non-stoichiometric, with an apparent valence greater than three, the actual valence change during charge and discharge can be greater than one.

Though impregnation with the less concentrated solutions is attractive from a uniformity and reproducibility point of view, the specific capacity even after twelve impregnations is less than that normally used in practical cells.

Table IX. Capacity, Weight-Gain and Utilization – Chemical Conversion, Positive Plates

	Number of Impregnations	Active Material, g/cm^2 A	B	C	Capacity, Ahr/cm^3 Theoretical	Measured*	Utilization, %
Saturated $Ni(NO_3)_2$							
PC1a	2	0.0529	0.0485	0.0504	0.141	0.173	122
b		0.0469	0.0501	0.0545		0.166	
PC2a	5	0.0984	0.0944	0.1011	0.328	0.314	91
b		0.0976	0.0914	0.0943		0.340	
PC3a	8	0.1282	0.1235	0.1250	0.457	0.452	99
b		0.1286	0.1284	0.1268		0.445	
PC4a	12	0.1523	0.1564	0.1479	0.583	0.491	84
b		0.1562	0.1542	0.1529			
50% Saturated $Ni(NO_3)_2$							
PC5a	2	0.0150	0.0155	0.0155	0.046	0.047	102
PC6a	5	0.0311	0.0351	0.0347	0.096	0.087	91
PC7a	8	0.0506	0.0484	0.0494	0.188	0.181	96
PC8a	12	0.0747	0.0730	0.0734	0.246	0.261	106

*Measured on piece A.

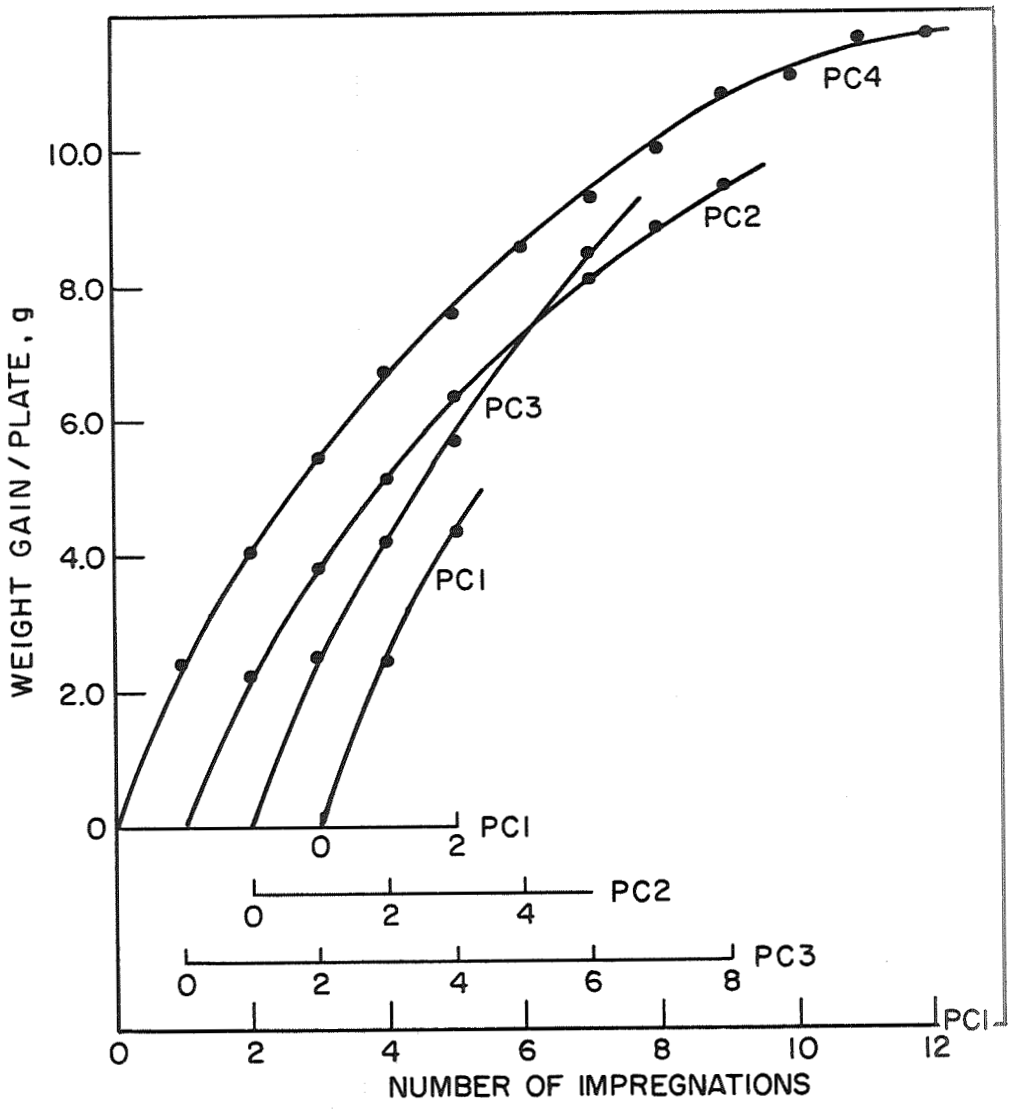

Fig. 7. Reproducibility of chemical conversion process – positive plates, saturated impregnation solution

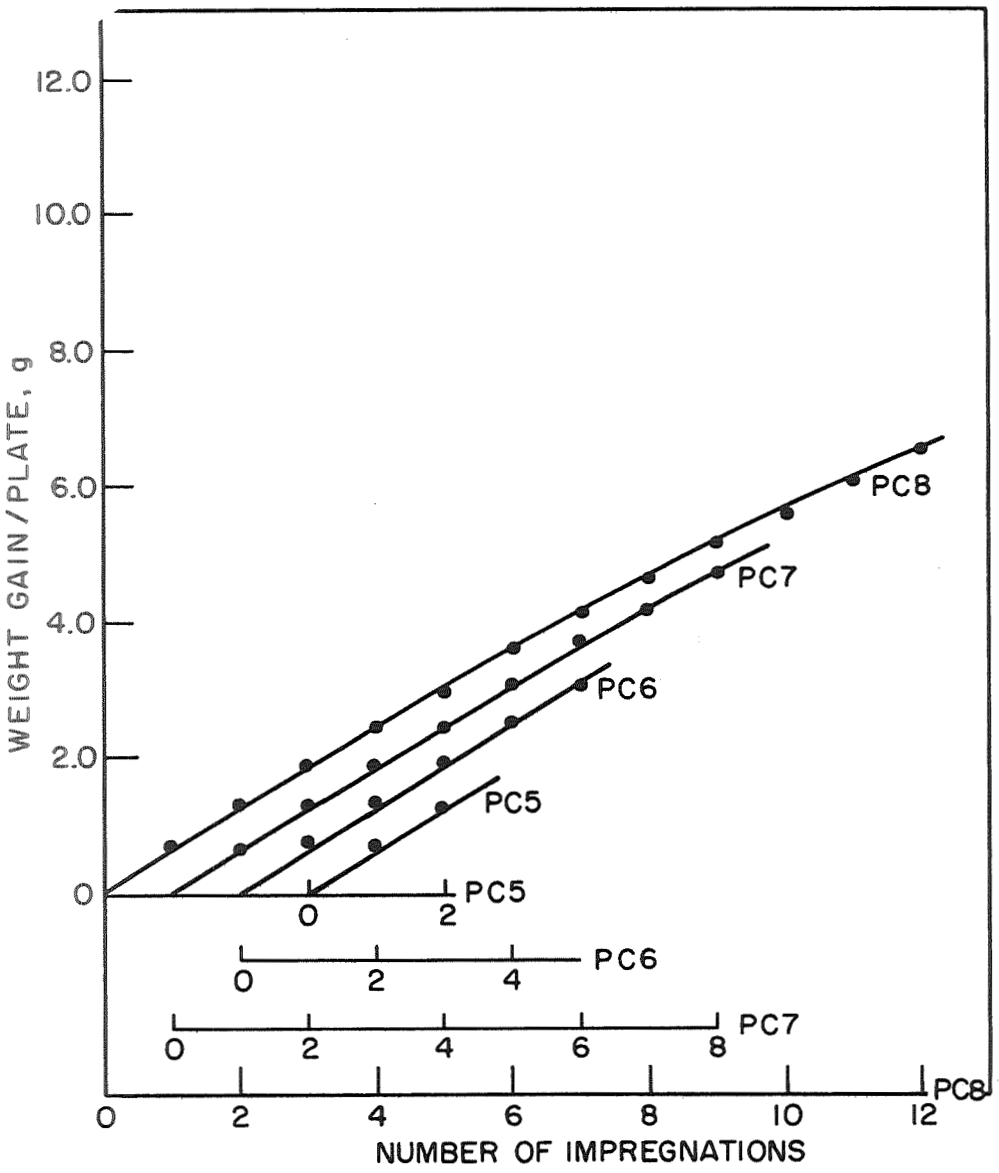

Fig. 8. Reproducibility of chemical conversion process – positive plates, 50% saturated impregnation solution

C. Modified Fleischer Process - Positive Plates

The modification to the process consisted of a drying step between impregnation with the nitrate and cathodization in KOH. The weight gains recorded were slightly greater than the Fleischer process, as were the measured capacities, but as is apparent from Table X both reproducibility and uniformity were not as good.

Table X. Capacity, Weight Gain and Utilization-Modified Fleischer Method, Positive Plates

	Number of Impregnations	Active Material, g/cm^2			Capacity, Ahr/cm^2		Utilization, %
		A	B	C	Theoretical	Measured	
PCF1	2	0.0389	0.0375	0.0356	0.181	0.118	65
PCF2	5	0.0807	0.0732	0.0759	0.343	0.307	90
PCF3	8	0.1158	0.1061	0.1072	0.344	0.344	86

D. Electrochemical Method - Positive Plates

The data obtained for positive plates prepared by the electrochemical method are summarized in Table XI. The uniformity of the loading was not good and for all except the 4M solution the plates impregnated for 20 min were more lightly loaded than the 10-min plates. The few duplicate experiments carried out showed poor reproducibility. The specific capacities were also quite low. Because of the poor uniformity and reproducibility, the complete series of duplicates was not completed nor was the characterization of the plates carried out comprehensively. Instead attention was focussed on the recently reported high temperature electrochemical impregnation process. These studies will be presented in future reports.

E. Fleischer Method - Negatives

A summary of the data on negative plates prepared by the Fleischer process is given in Table XII. Plates NF1 through NF4 were cathodized at 150 mA/cm^2 and plates NF5 through NF8 at 300 mA/cm^2. Reasonable reproducibility was obtained in the duplicate preparations in most cases, the largest differences being observed in the low loading plates. These figures must, however, be regarded more circumspectly than those for the positive plates, since in these preparations the cathodic current can, in addition to reducing nitrate, convert cadmium hydroxide to cadmium. Thus, the active material in the green plate is a mixture of cadmium and cadmium hydroxide, the relative proportions in different areas of the plate being dependent on the current distribution across the plate. Under these circumstances, it is to be expected

Table XI. Capacity, Weight Gain and Utilization - Electrochemical Conversion, Positive Plates

	Time, min	Active Material, g/cm^2 A	B	C	Capacity, Ahr/cm^2 Theoretical	Measured	Utilization, %
				170 mA/cm^2 2M, 25 °C			
PE1	5	0.0202 (whole plate)			0.101	0.081	80
PE2	10	0.0364 (whole plate)			0.126	0.104	82
PE3	20	0.0631	0.0649	0.0671	0.228	0.166	73
				340 mA/cm^2, 2M, 25 °C			
PE4	5	0.0366	0.0346	0.0370	0.128	0.091	71
PE5	10	0.0568	0.0489	0.0598	0.200	0.150	75
PE6	20	0.0483	0.0522	0.0522	0.170	0.135	79
				420 mA/cm^2, 2M, 25 °C			
PE7	5	0.0272	0.0393	0.0359	0.120	0.110	92
PE8	10	0.0610	0.0606	0.0630	0.224	0.165	74
PE9	20	0.0614	0.0557	0.0560	0.218	0.164	75
				680 mA/cm^2, 2M, 25 °C			
PE10	5	0.0562	0.0529	0.0589	0.187	0.151	81
PE11	10	0.0449	0.0397	0.0478	0.164	0.116	69
				340 mA/cm^2, 4M, 25 °C			
PE12	5	0.0484	0.0539	0.0472	0.172	0.132	77
PE13	10	0.0605	0.0668	0.0703	0.212	0.182	86
PE14	20	0.0781	0.0804	0.0814	0.273	0.257	94

Table XII. Capacity, Weight-Gain and Utilization – Fleischer Method, Negative Plates

	Number of Impregnations	Active Material, g/cm^3			Capacity Ahr/cm^3		Utilization, %
		A	B	C	Theoretical	Measured*	
150 mA/cm^2							
NF1a	2	0.0469	0.0649	0.0524	0.304	0.207	68
b		0.0497	0.0459	0.0516	0.275	0.212	77
NF2a	5	0.1337	0.1259	0.1208	0.658	0.492	75
b		0.1255	0.1353	0.1270	0.677	0.461	69
NF3a	8	0.1662	0.1699	0.1632	0.808	0.590	74
b		0.1703	0.1673	0.1642	0.790	0.610	77
NF4a	12	0.2018	0.2121	0.1928	0.956	0.726	76
b		0.2230	0.1943	0.1904	0.922	0.663	72
300 mA/cm^2							
NF5a	2	0.0430	0.0664	0.0682	0.279	0.213	76
b		0.0530	0.0545	0.0572	0.343	0.233	68
NF6a	5	0.1162	0.1198	0.1360	0.601	0.474	79
b		0.1127	0.1159	0.1115	0.725	0.426	60
NF7a	8	0.1563	0.1563	0.1635	0.823	0.593	72
b		0.1533	0.1508	0.1512			
NF8a	12	0.1807	0.1915	0.2006	1.179	0.576	49
b		0.2042	0.2162	0.2069			

* Measured on piece A.

that there would be greater disparity between the figures for the 300 mA/cm^2 preparations than those for the preparations at 150 mA/cm^2. This is not apparent from the figures in Table XII but if we examine the reproducibility in terms of the weight gain per impregnation cycle (Figs. 9 and 10), we note that at 150 mA/cm^2 there is more scatter than was observed for the positives and at 300 mA/cm^2 considerable variations in weight gain occur.

Because of the distribution of current density during cathodization, it is not possible to assess the uniformity of the distribution of active material throughout a particular plate from the figures presented in Table XII. However, chemical analyses were carried out on Sections A and C of plates NF1 to NF4 to determine the relative amounts of cadmium and cadmium hydroxide. These figures were then converted to give a value for the weight of cadmium per unit area in each section. The results derived from the chemical analyses are presented in Table XIII. As will be noted, excellent agreement with one exception is obtained in terms of both uniformity and reproducibility at all loadings. Plate NF8 which had the largest total cadmium pickup gave a quite low capacity because of poor utilization. In general, the utilization ranged from 68 to 79% without any apparent pattern. The capacities after five impregnations or more were in excess of the commonly used capacity of ~0.4 Ahr/cm^3. The theoretical capacities listed in Table XII are based on chemical analysis of the plate to define the total cadmium content. The measured capacities were reasonably consistent except for the most heavily loaded plates.

Table XIII. Distribution of Cadmium g/cm^2-Fleischer Method, Negative Plates

	Number of Impregnations	Cadmium, g/cm^2	
		Section A	Section C
NF1a	2	0.047	0.046
NF1b	2	0.048	0.047
NF2a	5	0.112	0.108
NF2b	5	0.116	0.114
NF3a	8	0.138	0.138
NF3b	8	0.203	0.132
NF4a	12	0.164	0.164
NF4b	12	0.158	0.165

F. Chemical Conversion - Negatives

The experimental measurements made on negative plates prepared by chemical conversion are recorded in Table XIV. Plates NC1 through NC4 were prepared with saturated cadmium nitrate as the impregnation solution. Plates NC5 through NC8 were prepared with an impregnation solution of half-saturated concentration. Again apart from the plates that received only two impregnation cycles, reasonable reproducibility was obtained between replicate

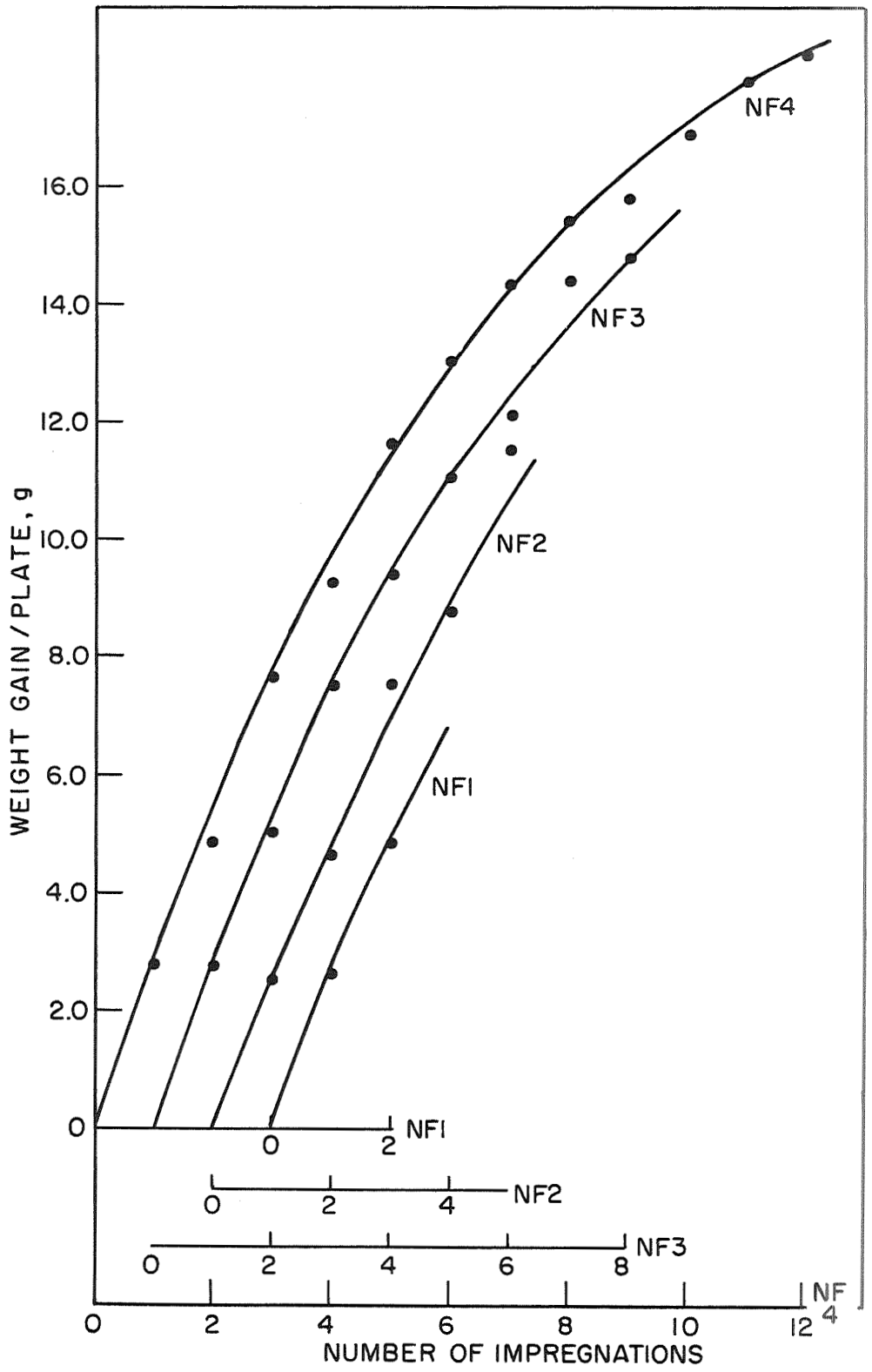

Fig. 9. Reproducibility of Fleischer process – negative plates cathodized at 150 mA/cm^2

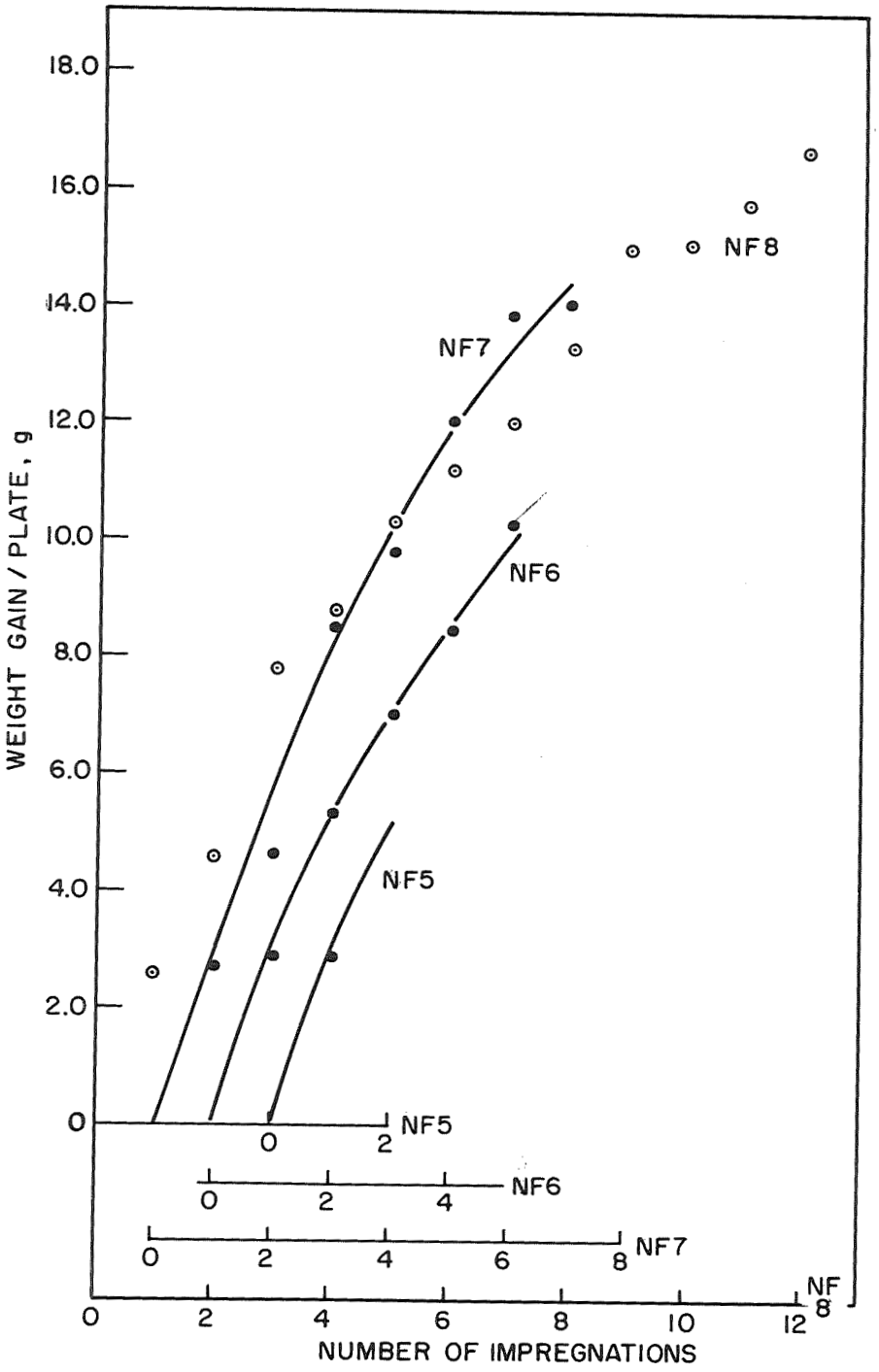

Fig. 10. Reproducibility of Fleischer process – negative plates cathodized at 300 mA/cm^2

Table XIV. Capacity, Weight-Gain and Utilization – Chemical Conversion, Negative Plates

	Number of Impregnations	Active Material, g/cm^2			Capacity, Ahr/cm^3		Utilization, %
		A	B	C	Theoretical	Measured*	
NC1a	2	0.0655	0.0622	0.0668	0.295	0.170	58
b		0.0583	0.0668	0.0669			
NC2a	5	0.1356	0.1417	0.1507	0.600	0.540	90
b		0.1465	0.1378	0.1423			
NC3a	8	0.1792	0.1628	0.1681	0.808	0.581	72
b		0.1786	0.1624	0.1608			
NC4a	12	0.1854	0.1821	0.1867	0.838	0.627	75
b		0.1813	0.1880	0.1912			
NC5a	2	0.0259	0.0253	0.0356	0.123	0.067	55
b		0.0280	0.0330	0.0419			
NC6a	5	0.0623	0.0584	0.0583	0.279	0.228	82
b		0.0606	0.0635	0.0708			
NC7a	8	0.0948	0.0893	0.0960	0.444	0.314	71
b		0.0977	0.0944	0.0916			
NC8a	12	0.1488	0.1371	0.1376	0.670	0.530	79
b		0.1447	0.1426	0.1388			

*Measured on piece A.

samples. Note that in this case there is no ambiguity with respect to the stoichiometry of the active material (cadmium hydroxide). Comparison of the weight gains after each impregnation cycle (Fig. 11 and 12) also indicates good reproducibility, possibly slightly better for the more concentrated solutions.

Uniformity of the distribution of active material is acceptable though the spread in values is greater than those observed with the positive plates and with the negatives prepared by the Fleischer method.

G. Electrochemical Method - Negative Plates

The data obtained for negative plates prepared by electrochemical impregnation are set out in Table XV. It is more difficult to assess the uniformity of the process from the weight per unit area of different sections because of the partial conversion of the hydroxide to metallic cadmium. The extent of the conversion could vary from area to area because of a nonuniform distribution of current density. The analyses showed a consistent conversion factor for a particular current density but all the measurements were made on the same section of each electrode. The recorded weight gains, however, show a random pattern as a function of section which leads one to believe that the observed spread is a result of the inherent nonuniformity of the method as practiced. It is believed that a higher degree of uniformity is possible with better control of the factors involved. Note that control of this process is more complex than the chemical or Fleischer processes because of the larger number of variables involved. We have opted to study the control of these factors for electrochemical impregnation at high temperatures. This will be reported on in the future.

H. Comparative Analysis of Impregnation Methods - Positives

1. Weight gain and capacity

A plot of weight gain and capacity against the number of impregnations for each preparation is presented in Fig. 13. The highest loading and highest capacity are obtained with the chemical conversion process using saturated solutions. The lowest loading and capacity also were observed for the chemical conversion process using less concentrated solutions. From this, we may infer that control of this process is quite dependent on control of solution concentration. This remark is probably equally true of the Fleischer process though we do not have the data to confirm it.

The two sets of plates prepared by the Fleischer process do not show a marked dependance on current density, though the higher current density does produce a slightly higher loading and slightly greater capacity for the same number of impregnations.

Of greater interest, however, are the capacities at equal loading that can be derived from the plots in Fig. 13. These are presented in Table XVI. At loadings of 4.0 and 6.0 g/plate, the capacities are almost identical and moreover the Ahr/g figure of 0.04 applies to all four preparations up to a loading of 6.0 g plate. Thus, the choice of method of positive plate

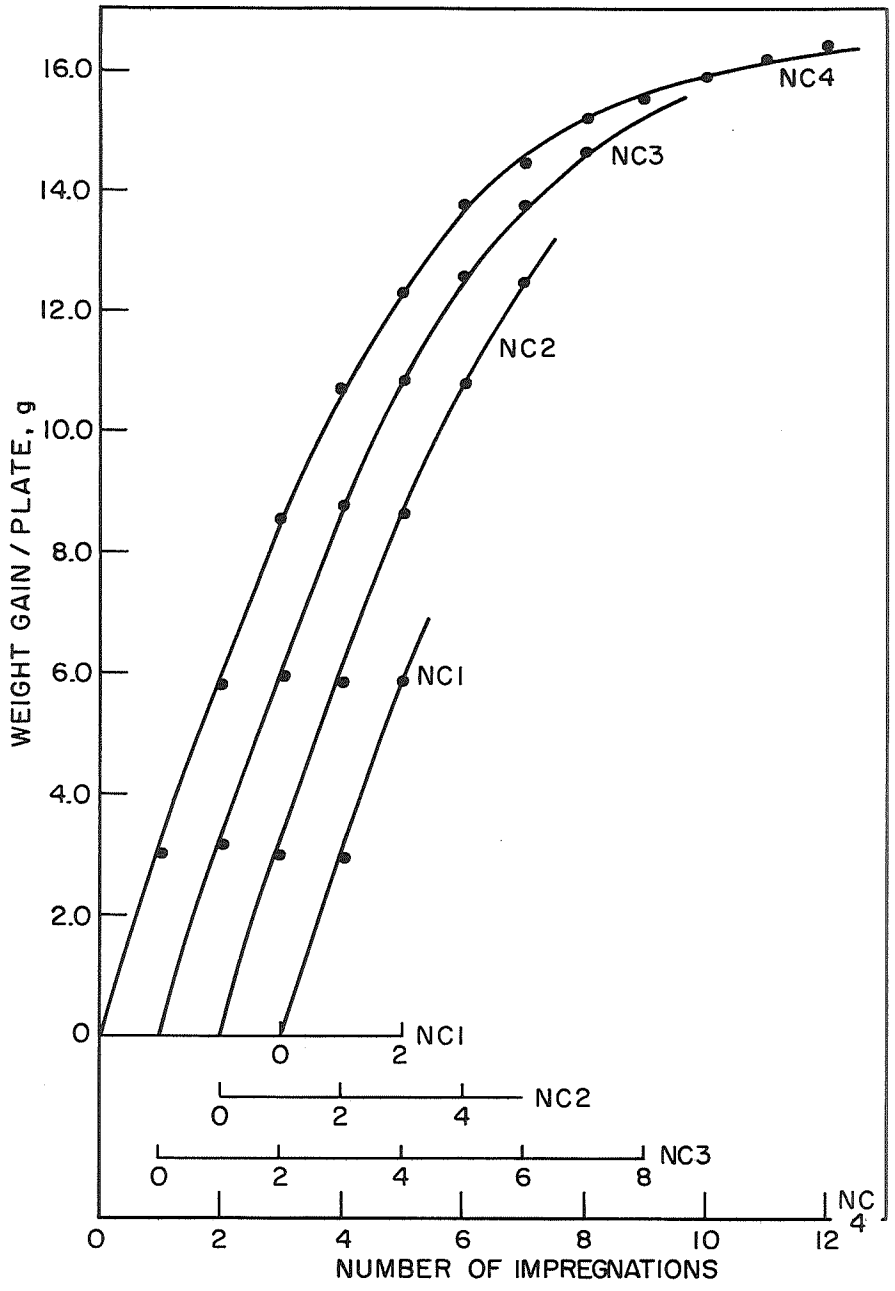

Fig. 11. Reproducibility of chemical conversion process – negative plates prepared with saturated impregnation solution

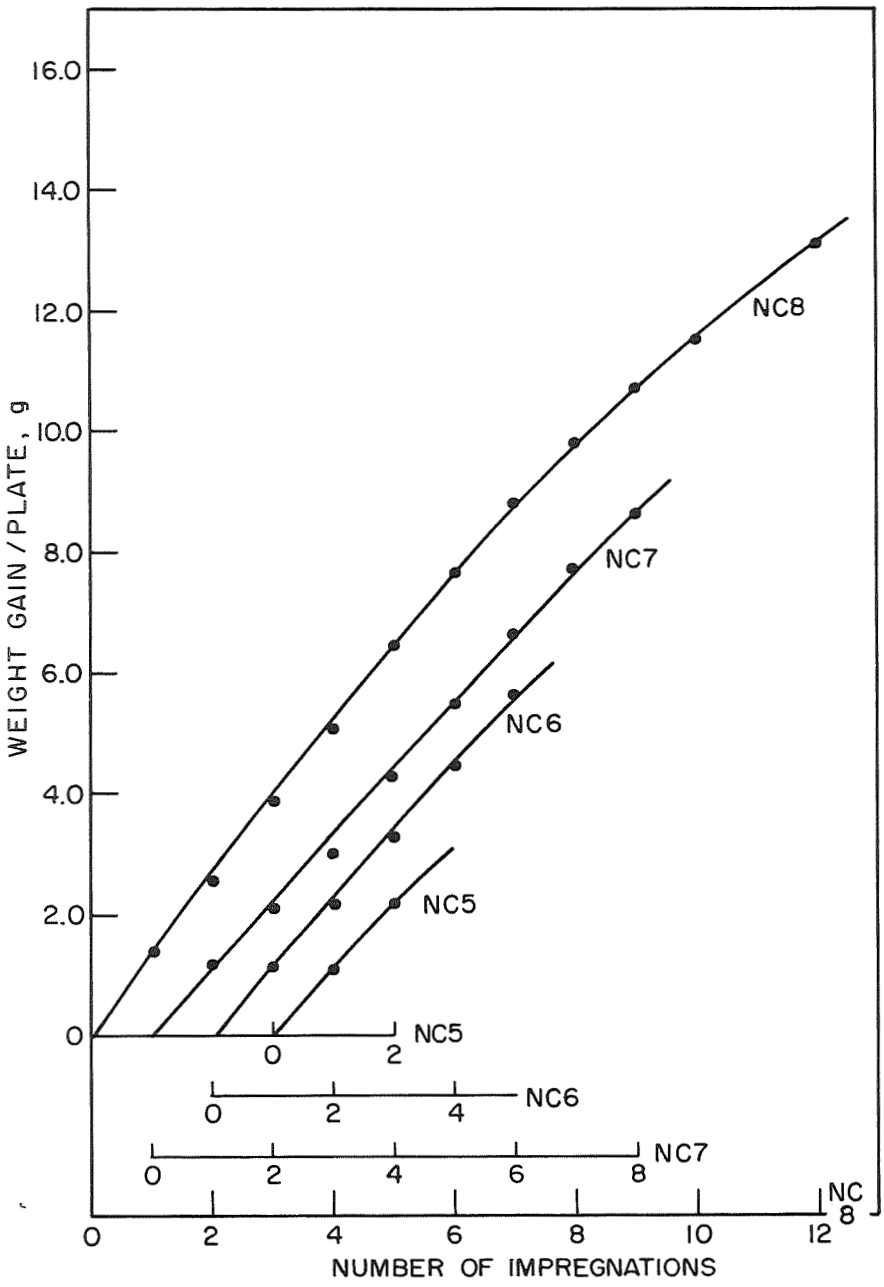

Fig. 12. Reproducibility of chemical conversion process – negative plates prepared with 50% saturated impregnation solution

Table XV. Capacity, Weight Gain and Utilization - Electrochemical Conversion, Negative Plates

	Time, min	Active Material, g/cm^2			Capacity, Ahr/cm^2		Utilization, %
		A	B	C	Theoretical	Measured	
		50 mA/cm^2, 2M, 25 °C					
EN1	10	0.0411	0.0399	0.0423	0.244	0.182	75
EN2	20	0.0524	0.0510	0.0564	0.299	0.239	80
EN3	20[1]	0.0503	0.0364	0.0425	0.221	0.175	79
EN4	20[1]	0.0751	0.0763	0.0823	0.417	0.326	78
EN5	30	0.0497	0.0550	0.0587	0.311	0.238	77
EN6	40[2]	0.1249	0.1200	0.1443	0.675	0.521	77
EN7	60	0.1729	0.1743	0.1999	(0.936)	0.311	35
		100 mA/cm^2, 2M, 25 °C					
EN8	5	0.0388	0.0372	0.0429	0.251	0.189	75
EN9	10	0.0398	0.0411	0.0423	0.241	0.188	78
EN10	20	0.0588	0.0513	0.0657	0.288	0.219	76
		150 mA/cm^2, 2M, 25 °C					
EN11	5	0.0384	0.0443	0.0403	0.252	0.212	84
EN12	10	0.0523	0.0562	0.0670	0.279	0.220	81

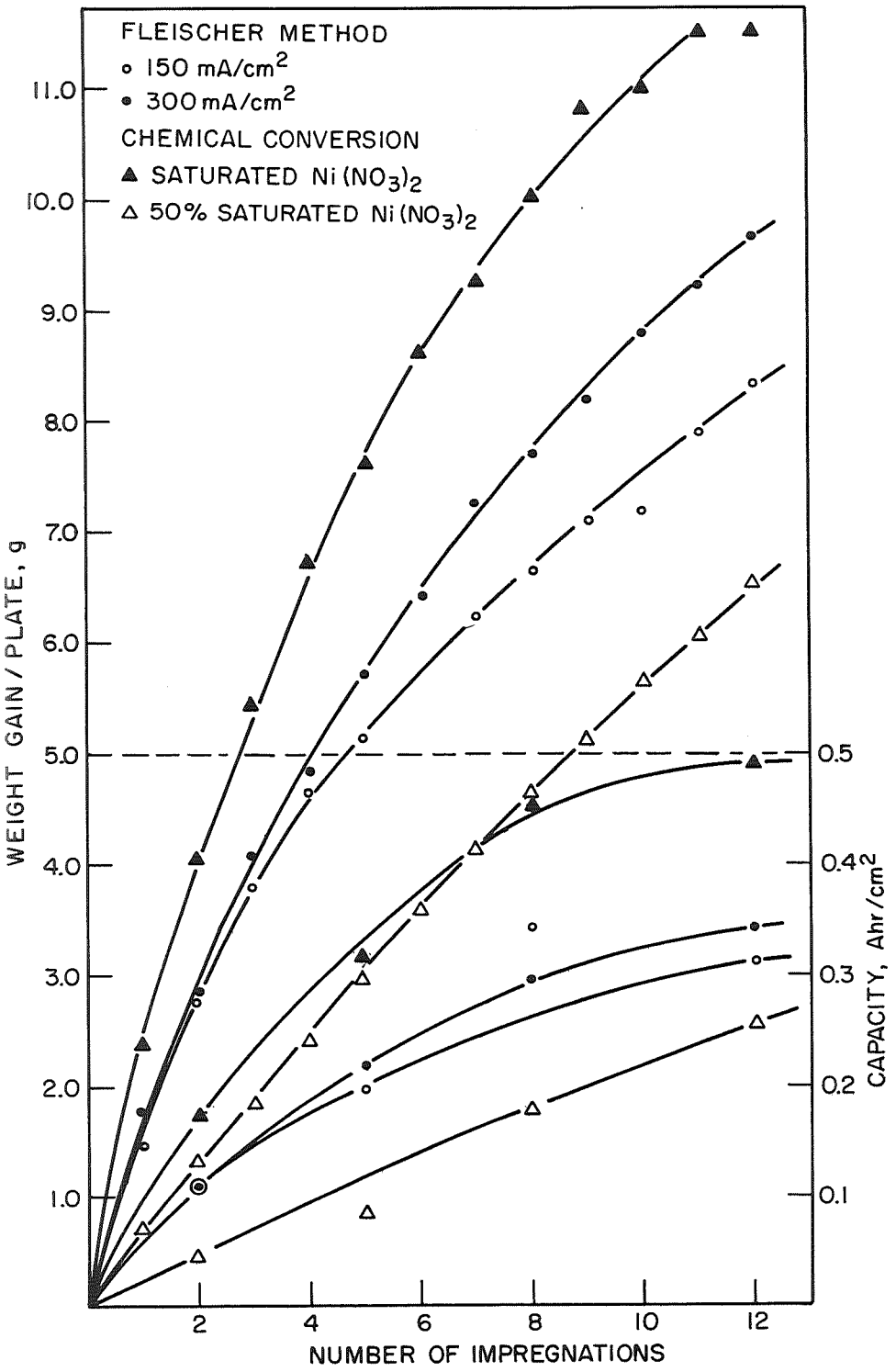

Fig. 13. Comparison of weight gain and capacity for Fleischer and chemical conversion methods – positive plates

preparation may be made entirely on the basis of which method gives the most uniform and reproducible product. It is therefore possible to choose an optimum number of impregnations and solution concentration to give the desired loading. The optimum number of impregnation cycles can be expressed in terms of a sufficient number to produce the desired leveling effect without being so great that the probability of a nonsystematic error is unnecessarily large.

Table XVI. Capacities in Ahr/cm^3 at Equal Loading - Positive Plates

Loading, g/plate	4.0	6.0	10.0
Chemical Conversion			
Saturated $Ni(NO_3)_2$	0.17	0.26	0.45
50% Saturated $Ni(NO_3)_2$	0.16	0.24	(0.38)*
Fleischer Method			
150 mA/cm^2	0.16	0.23	(0.33)*
300 mA/cm^2	0.16	0.23	(0.35)*

*Projected figures.

Electrochemical impregnation at room temperature did not give plates of uniformity and reproducibility comparable with either the chemical conversion or Fleischer process. This situation will be reexamined when the high temperature electrochemical impregnation process has been fully evaluated.

2. Miscellaneous factors

It is of interest to examine some of the incidental facts that can be derived from the data collected. For example, it is apparent (Table XVII) that there is more plaque corrosion during chemical conversion than in the Fleischer process (Table XVIII). Two factors probably influence this effect. The drying step of chemical conversion in essence involves prolonged contact with nitric acid at elevated temperatures. Also the cathodization associated with the Fleischer process maintains the plaque at a potential where no corrosion of nickel can take place. During chemical conversion, any oxygen present during the KOH treatment can induce corrosion of the nickel plaque where it is not fully protected by a passive film. The apparent decrease in plaque corrosion with increase in the number of impregnation cycles is probably an artifact relating to the sensitivity of the analytical procedures.

This latter comment also applied to the determination of the water content of the active material (Table XVII and XVIII), though it does appear that the water content of the Fleischer

Table XVII. Plaque Corrosion – Water Content and Surface Area, Positive Plates, Fleischer Method

	Number of Impregnations	Plaque Corrosion, %	Water Content of Active Material, %	Surface Area, m^2/g active material	Utilization %
PF1a	2	4	0	152	68
PF2a	5	0	15	69	81
PF3a	8	2	12	53	91
PF4a	12	0	16	54	90
PF5a	2	3	9	129	94
PF6a	5	0	8	95	86
PF7a	8	0	8	68	91
PF8a	12	0	9	46	87

Table XVIII. Plaque Corrosion – Water Content and Surface Area, Positive Plates, Chemical Conversion

	Number of Impregnations	Plaque Corrosion, %	Water Content of Active Material, %	Surface Area, m^2/g active material	Utilization, %
PC1a	2	8	12	118	122
PC2a	5	8	11	80	91
PC3a	8	4	13	63	99
PC4a	12	7	7	38	84
PC7a	8	3	7	–	96
PC8a	12	–	12	–	106

plates prepared at 150 mA/cm^2 is greater than those prepared at 300 mA/cm^2. There is also a link between water content and utilization. Those plates with a high water content also showed the highest utilization factor.

Lastly, we may make a comparison of the surface area of the active material in various plates. Expressed in terms of m^2/g of active material, the surface area decreases as the loading increases (Fig. 14). This behavior is different from that of Jost and Rufenacht[31] who claimed no decrease in surface area as the loading was increased. However, this difference could be related to the morphology of the active material. The morphological differences associated with the two different methods of preparation are apparent in Fig. 14 in that two distinct groupings of points can be discerned.

A brief examination was made of the effect of thickness on reproducibility and uniformity. The results are presented in Table XIX. The thicker plaque gave better uniformity but it is considered that this probably reflects the difference in quality of plaques rather than any fundamental effect. The measured capacities in Ahr/cm^3 were quite uniform.

I. Comparative Analysis of Impregnation Methods - Negatives

A comparison of weight gain and capacity for the different conditions of negative plate preparation is given in Fig. 15. Up to a loading of 14 g/plate, the chemical conversion process with saturated cadmium nitrate provides the greatest weight gain. At higher loadings, however, the Fleischer method in which some of the cadmium hydroxide is reduced to the more dense cadmium metal provides a greater void volume in the plate so that it is able to pick up more active material. This pattern is reflected in the capacities also. A surprising feature is that in the Fleischer process the cathodizing at 150 mA/cm^2 is more efficient in terms of weight gain than cathodizing at 300 mA/cm^2. This could be related to the rate of gas formation in the pore structure.

Table XIX. Capacity, Weight Gain, and Utilization as a Function of Thickness

Thickness, cm	Weight of Active Material, g/cm^3			Capacity, Ahr/cm^3		Utilization, %
	A	B	C	Theoretical	Measured	
0.0660	1.369	1.000	1.133	0.326	9.294	91
0.0732	1.042	0.933	1.120	0.300	0.300	100
0.0832	1.144	1.149	0.331	0.331	0.303	92
0.0879	1.088	1.065	1.083	0.305	0.318	104

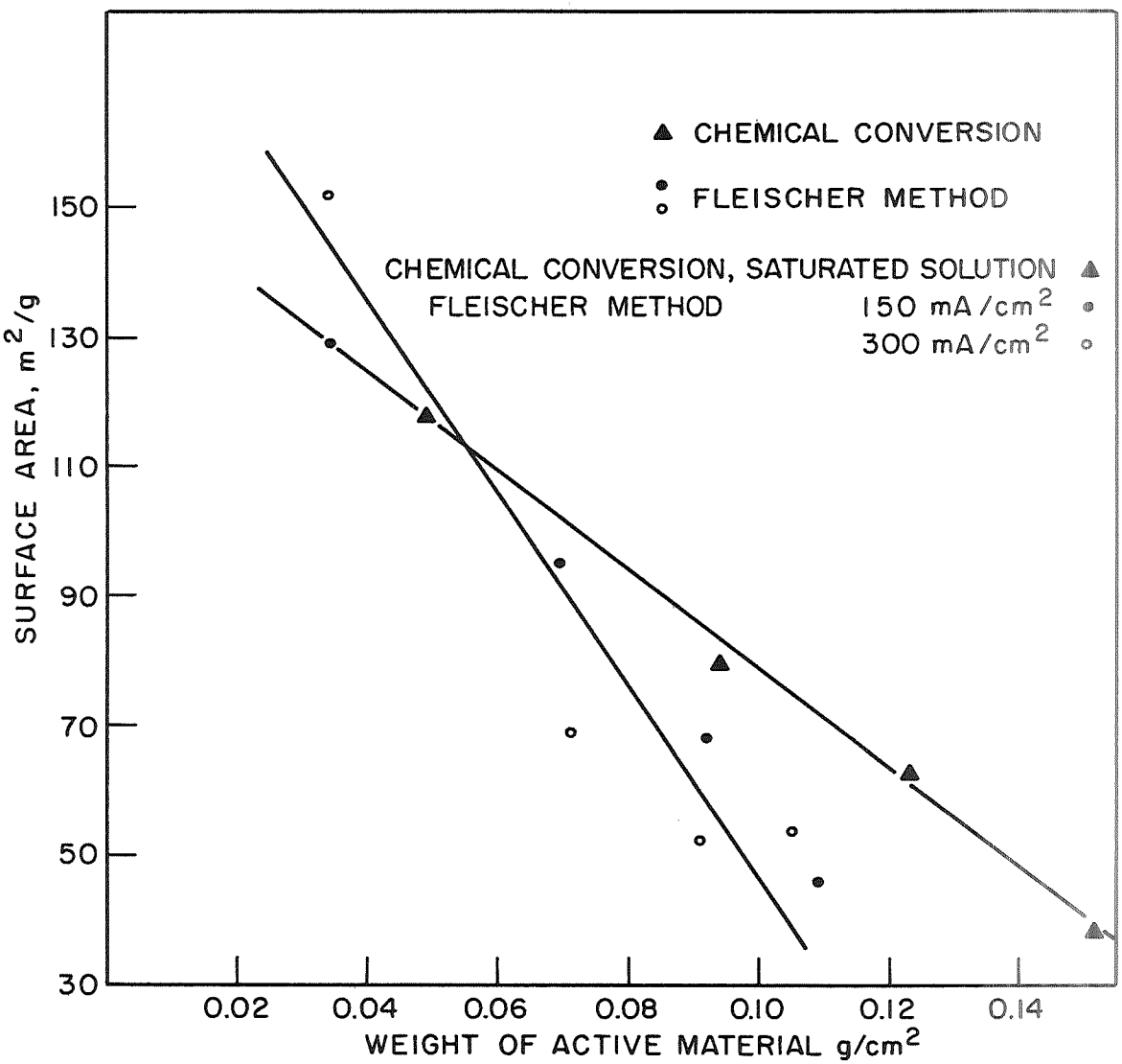

Fig. 14. Surface area as a function of weight gain

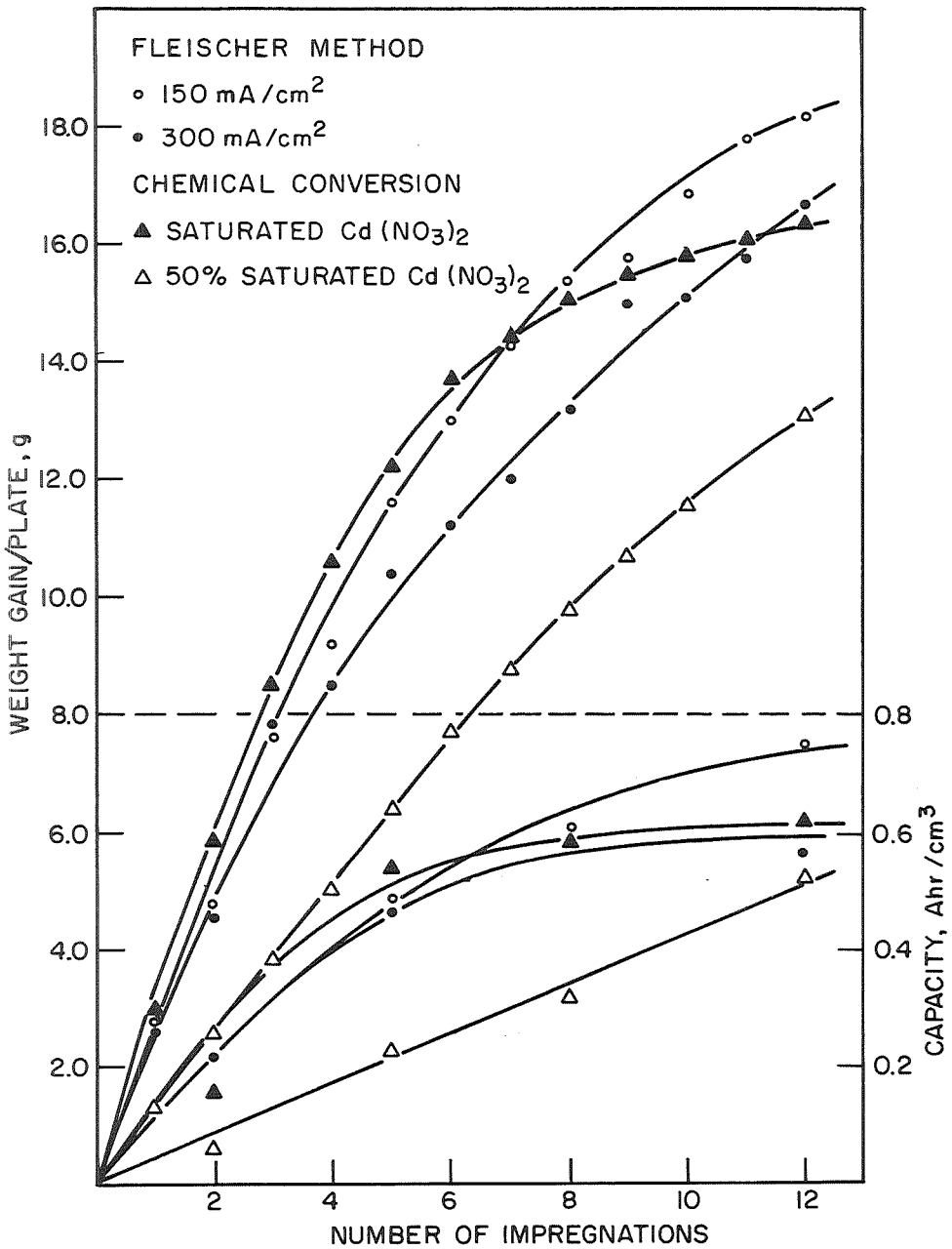

Fig. 15. Comparison of weight gain and capacity for Fleischer and chemical conversion methods – negative plates

However, in terms of the specific capacities at equal loadings (Table XX), the 300 mA/cm^2 figure for a 10-g loading is higher than the 150 mA/cm^2 and slightly higher than the chemical conversion. This is probably a result of differences in the morphology of the active material which is of greater importance than in the case of the positive active material. Any advantage in the Fleischer process at 300 mA/cm^2 in this respect will more than likely be offset by the much better reproducibility observed with the lower current density or in the chemical conversion process.

Table XX. Capacities in Ahr/cm^3 at Equal Loading - Negative Plates

Loading, g/plate	4.0	6.0	10.0	16.0
Chemical Conversion				
Saturated $Cd(NO_3)_2$	0.17	0.26	0.44	0.62
50% Saturated $Cd(NO_3)_2$	0.13	0.20	0.35	-
Fleischer Method				
150 mA/cm^2	0.17	0.25	0.40	0.66
300 mA/cm^2	0.18	0.27	0.46	0.60

V. CONCLUSIONS

The stated objectives of this phase of the program were to define systematic procedures for the preparation of uniform and reproducible nickel cadmium battery plates. In an ongoing program with further evaluation of these components, it is perhaps premature to be too definite at this stage. However, the work presented above cannot be allowed to stand without the salient features being summarized. Based on the above data, using the experimental techniques practiced at Tyco, it would appear that of the three processes considered the chemical conversion process provides the most reproducible and uniform materials. The negative plates may be prepared most conveniently using saturated cadmium nitrate solution for impregnation. For the positive plates, the less concentrated impregnation solution provided the more uniform and reproducible plates though an inordinate number of impregnations would be required to reach normal specific capacities. The electrochemical impregnation method is considerably less reproducible than the other methods but it is probable that not all the controlling variables were kept constant.

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APPENDIX I. Analytical Procedure for Negative Plates

The analytical procedures described in the main text of this report were directed at the specific objectives of the program, i.e., the determination of the total quantity of active material present in the plate so that we might define utilization. In many cases, the analyses were carried out on plates in the discharged state after formation, also we were rarely interested in the relative amounts of material in the charged and discharged states. The significance of these two factors is that there was no restriction on handling the plates in air and that the quantity of metallic cadmium in the plates at the time of analysis was usually small. Under these circumstances, the color changes observed during the complexometric titrations as described in this report may not be typical of those in the presence of larger quantities of metallic cadmium.

We will therefore describe in detail the procedures as they were practiced in this program and indicate the modifications that might be required in the analysis of charged plates. Studies of the procedures for charged plates are currently being made at NASA Goddard. These will be described in a forthcoming NASA Goddard X Document.

In principle, the method used provides for the separate determination of the charged and discharged states of the negative plates. The discharged state is first dissolved in a solution of ammonium chloride and ammonium hydroxide and then determined by EDTA titration. The metallic cadmium remaining in the plaque is then dissolved along with the nickel in nitric acid and the cadmium determined by EDTA titration according to the following procedures.* (Although EDTA can be considered as a primary standard, it is probably more convenient to standardize against a known cadmium solution.)

Principle

Cadmium hydroxide, the discharged state of a negative electrode, is extracted into a solution of ammonium chloride and ammonium hydroxide. Metallic cadmium, the charged state, remains in the nickel plaque. The amount of charged cadmium is determined after acid solution.

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*These procedures are reproduced from a copy of a report of Dolores Moore provided to us by Dr. A. Fleischer.

Reagents

(1) Standard Cadmium: 1 ml. ≅ 2.5 mg. cadmium. Dissolve 4.077125 grams anhydrous cadmium chloride in water and dilute to 1 liter.

(2) EDTA Solution .05M: Dissolve 18.6 grams disodium ethylenediaminetetraacetate in distilled water and dilute to 1 liter. For a .01M EDTA solution dilute 100 ml. .05M EDTA to 500 ml. with distilled water.

(3) Buffer (Mussprat Solution): Dissolve 54 grams ammonium chloride in approximately 300 ml. distilled water. Add 350 ml. ammonium hydroxide and dilute to 1 liter with distilled water. pH = 10.

(4) 10% Formaldehyde Solution: Dilute 28 ml. 36% formaldehyde to 100 ml. with distilled water.

(5) 10% Sodium Cyanide Solution: Dissolve 25 grams sodium cyanide in 250 ml. distilled water.

(6) Eriochrome Black T: Mix 0.125 grams Eriochrome Black T with 50 grams sodium chloride.

Standardization of EDTA Solution

Transfer known amounts of cadmium to 250 ml. beakers. Dilute to approximately 100 ml. with distilled water. Adjust the pH to approximately 10 with ammonium hydroxide. Before removing the sample from the pH meter, add 10 ml. buffer and stir sample. Remove sample and add 5 ml. 10% sodium cyanide. Place beaker on a magnetic stirrer and add enough Eriochrome Black T to impart a medium blue color to the sample solution. Add sufficient 10% formaldehyde solution until a wine-red color is obtained and add approximately 1-2 ml. in excess. Titrate immediately with EDTA solution until a permanent blue color is obtained. Calculate EDTA factor, milligrams of cadmium per milliliter of EDTA.

Analysis of Sample

A. Cadmium Hydroxide - Discharged State

(1) Samples containing approximately 1 gram cadmium hydroxide:

Weigh the samples to be analyzed. The samples should be free of electrolyte and dry. Add 10 grams ammonium chloride to approximately 200 ml. distilled water in a 400 ml. beaker. Heat the solution to approximately 70-80 °C. and add 75 ml. ammonium hydroxide. Place samples in their respective beakers. Continue heating for 2 hours at 70-80 °C. with occasional stirring, adding 25 ml. ammonium hydroxide after the first hour of extraction to replace that which is lost by evaporation. (See Note 1). Cool and transfer the extract to a 500 ml. volumetric flask. Wash nickel plaque and transfer washings to flask. Dilute to volume with distilled water. Save nickel plaque for analysis in Section B. Transfer an aliquot to a 250 ml. beaker and dilute to approximately 100 ml. with distilled water. Adjust the pH to approximately 10 with ammonium hydroxide and proceed as for the standardization of EDTA.

(See Note 3). Calculate the amount of cadmium present in the discharged state.

(2) Samples containing 1-4 grams cadmium hydroxide:

To 600 ml. beakers add approximately 400 ml. distilled water and 10 grams of ammonium chloride for each gram of cadmium hydroxide present in the sample. A rough estimate of the amount of cadmium and cadmium hydroxide in a sintered plaque is obtained by multiplying the weight of the electrode by 50%. Heat the solution to 70-80 °C. and add 100 ml. 28% ammonium hydroxide. Place samples in respective beakers. Continue heating at 70-80° with occasional stirring for approximately 2 hours. After one hour of extraction add 50 ml. ammonium hydroxide. (See Note 1.) Samples containing 3 or 4 grams cadmium hydroxide must be extracted twice with a fresh solution of ammonium hydroxide and ammonium chloride. Transfer the extracts to a 1000 ml. flask, wash the nickel plaque with distilled water transferring the washings to the flask. Dilute to volume. Transfer an aliquot to a 250 ml. beaker and proceed as for standardization of EDTA. (See Note 3.) Calculate the amount of cadmium present in the discharged state.

(3) Samples containing more than 4 grams cadmium hydroxide:

Weigh the electrode to be analyzed. It must be free of electrolyte and dry. Cut a sample containing 1-4 grams cadmium hydroxide from the electrode and weigh the sample. Proceed as described above. Calculate the percent by weight of cadmium in the sample portion.

$$\text{Percent Cadmium} = \frac{\text{Wt. cadmium} \times 100}{\text{Sample wt.}}$$

Calculate the total cadmium in the electrode in the discharged state.

Total Cd in discharged state = weight electrode × percent cadmium

B. Cadmium - Charged State

Dissolve the nickel plaque loosely broken up by hand and separated from the screen or perforated sheet substrate in 1:1 nitric acid. Evaporate to a syrupy consistency to remove the majority of the excess acid. (Note 2.) Dissolve the sample in distilled water. Cool and dilute to a suitable volume. Transfer an aliquot containing no more than 0.5 gram of nickel to a 250 ml. beaker (approximately 50% of the weight of the electrode containing a sintered plaque is nickel). Dilute to approximately 100 ml. with distilled water and adjust the pH to approximately 10 with ammonium hydroxide. Before removing the sample from the pH meter, add 10 ml. buffer and stir. If the sample remains cloudy, add an additional 10 ml. of buffer. Remove sample and add 5 ml. 10% sodium cyanide for 0-0.5 grams nickel and 5 ml. for each addition 0.1 gram of nickel present. Place sample on a magnetic stirrer and add enough Eriochrome Black T to give a medium blue or green color to the sample solution. The color depends upon the amount of nickel present. Add enough 10% formaldehyde to liberate

the cadmium (wine-red color) and approximately 1-2 ml. in excess. Titrate immediately with standard EDTA solution until a permanent blue or green color is obtained. (Note 3.) Calculate the amount of cadmium present in charged state.

Calculation

(1) $$\text{EDTA factor} = \frac{\text{mg. cadmium}}{\text{m}\ell\ \text{EDTA}}$$

(2) Cadmium in discharged state:

$$\frac{\text{ml. EDTA} \times \text{EDTA factor} \times \text{volume of sample}}{\text{ml. of aliquot}}$$

(3) Cadmium in charged state:

$$\frac{\text{ml. EDTA} \times \text{EDTA factor} \times \text{volume of sample}}{\text{ml. of aliquot}}$$

(4) Percent cadmium in discharged state:

$$\frac{\text{Cadmium in discharged state}}{(\text{Cadmium in discharged state} + \text{cadmium in charged state})}$$

(5) Percent cadmium in charged state:

$$\frac{\text{Cadmium in charged state}}{(\text{Cadmium in discharged state} + \text{cadmium in charged state})}$$

(6) Cadmium hydroxide in discharged state:

Grams cadmium in discharged state $\times$ 1.30264.

Note 1:

The solutions of samples in section A must not be allowed to lose all their excess ammonium hydroxide, since the charged cadmium will be attacked.

Note 2:

The samples to be analyzed in section B must be free of excess acid.

Note 3:

Excessive additions of reagents must be avoided.

Note 4:

If only total cadmium is to be determined eliminate section A and proceed as in section

B. Alternate method: Discharge the cadmium completely at the 0.50 rate by continuing the discharge for 15 minutes after gassing begins. Wash the electrode free of eleclrolyte, dry at 60° overnight, weigh and proceed as in section A eliminating section B. After extraction wash plaque well and dry at 60 °C. overnight. The amount of cadmium hydroxide is determined by weight difference.

For analysis of plates in the charged state, the following additional precautions are necessary. From the time the plate is removed from the cell it must be kept out of contact with air. Washing should be carried out with deoxygenated water and drying and weighing carried out in an inert atmosphere. Similarly the extraction in Mussprat solution must be carried out with N_2 bubbling through the solution. After the dissolution of the $Cd(OH)_2$, there is no further requirement to protect the metallic cadmium from oxidation and the plaque may be handled in air. There is the possibility that the metallic cadmium could be in a sufficiently finely divided state to be pyrophoric. Should the plate burn there could be significant losses of cadmium. It is probably advisable to arrange slow exposure to air, e.g., by allowing slow drying at room temperature.

A further complication with plates based on a nickel plated iron substrate is the presence of iron in solution during the analysis for metallic cadmium. In the small number of analyses of this type that we have carried out, we have separated the porous mass from the substrate prior to dissolution in nitric acid. This does not eliminate iron completely but the residual amount is easily removed by filtration of the precipitate formed when the pH is first adjusted to 10. There are indications however that larger quantities of iron, i.e., the amounts present if the substrate is not separated physically, are not removed completely by the above procedure and produce complications in the color changes in the EDTA titration of cadmium. This aspect will be discussed in detail in the Goddard X Document.

APPENDIX II. Analytical Procedure for Positive Plates

The following is a step by step procedure for the analysis of positive plates in the discharged state. The active material is extracted under controlled potential conditions so that the nickel substrate is not attacked. In addition to the weight loss of the plaque, the total quantity of nickel extracted is determined by gravimetric analysis. This permits the calculation of the water content of the active material by the difference between the weight loss on extraction and the quantity of $Ni(OH)_2$ determined gravimetrically. A comparison of the weight per unit area of the plaque after extraction with the equivalent figure for the plaque prior to impregnation provides a figure for the extent of plaque corrosion during impregnation and cycling.

The plate to be analyzed is weighed and its geometrical area measured. The size of sample is chosen such that $Ni(OH)_2$ content is of the order of 0.5 g (typically ~3 cm^2 of 0.030-in.-thick plate). A long nickel tab is then attached to the sample to the existing tab or a previously prepared area of exposed screen or perforated sheet. The sample is then weighed again to permit the calculation of the weight loss on extraction without attempting to detach the nickel tab.

The extraction of the active material is carried out in Mussprat solution, the composition of which is defined in Appendix I. Approximately 200 ml of solution are placed in a 250 ml four-necked flask and heated to ~ 70°C under a N_2 atmosphere. To permit extraction under controlled potential conditions, a counterelectrode of platinum gauze and a dynamic hydrogen reference electrode are set up in the four-necked flask. [The concept, fabrication and mode of operation of the dynamic hydrogen electrode are described by Giner in J. Electrochem. Soc., 111, 377 (1964)].

The sample is introduced into the solution and its potential controlled at 25 mV positive to the dynamic hydrogen electrode with a potentiostat. The solution quickly assumes a blue color and after 1 hr is replaced with a fresh solution prepared in an identical manner to the routine described above. Nitrogen is bubbled briskly through the solution during the extraction to sweep out the small quantities of oxygen produced at the counterelectrode. One replacement of the Mussprat solution is usually sufficient to extract all the active material. However, for complete certainty, a third solution should be used to determine if there is a further loss in weight of the plaque.

The extraction solutions can normally be combined in a 500-ml volumetric flask. After dilution to a known volume, samples of the solution are analyzed for their nickel content using dimethyl glyoxime (DMG). The total nickel extracted from the plate can then be calculated. The plaque is also weighed after washing and drying.

We may then calculate the following:

1. % Wt loss on extraction = $\frac{\text{Weight loss}}{\text{Sample weight}} \times 100$

2. % $Ni(OH)_2$ in active material
   = $\frac{\text{Wt of } Ni(OH)_2 \text{ calculated from DMG determination}}{\text{Weight loss by extraction}} \times 100$

3. % H_2O in active material
   = $\frac{\text{Wt loss on extraction - wt } Ni(OH)_2}{\text{Weight loss by extraction}} \times 100$

4. % Plaque corrosion
   = $\frac{\text{Wt/unit area before impregnation-Wt/unit area after extraction}}{\text{Wt/unit area before impregnation}} \times 100$